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TABLES OF BOND AND RESONANCE ENERGIES
FOR ESTIMATING STANDARD HEATS
OF FORMATION

WILBUR F. OFFTERMATT

1953

TABLES OF BOND AND RESONANCE ENERGIES
FOR ESTIMATING STANDARD HEATS OF FORMATION

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of
Aeronautical Engineer

California Institute of Technology
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ABSTRACT

Tables of bond and resonance energies have been redetermined by using the most recent thermochemical data available. The use of the data is illustrated for the calculations of standard heats of formation of chemical compounds, including propellants.

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TABLES OF BOND AND RESONANCE ENERGIES FOR ESTIMATING STANDARD HEATS OF FORMATION

I. INTRODUCTION

Thermochemistry is concerned with methods for evaluating heat content or enthalpy changes in chemical reactions. Representative applications of thermochemical methods in jet propulsion engineering involve the theoretical calculation of rocket performance. In this connection, it is of primary importance to know the heats of formation of chemical compounds.

In any process, it is possible to measure only changes in heat content rather than absolute values. Hence, it is necessary to choose a standard state or a reference state to serve as a uniform basis for comparing heats of formation. The standard heat of formation of a given substance is defined as the heat evolved when one mole of the substance is formed from the elements in their respective standard states at 298.16°K and zero pressure. For ideal gases, the heat of formation defined in this way is equal to the heat of formation at a pressure of one atmosphere. For most real gases, the difference between the heats of formation at zero pressure and at one atmosphere is very small. The standard state for each element is the state in which it is most stable at 25°C . and 1 atm. pressure; i. e., the gaseous state for H_2 and N_2 , the liquid state for Hg, crystalline graphite for carbon, etc.

For chemical compounds for which the heats of formation are not known, it is frequently possible to estimate the standard heats of formation by the use of tables of bond energies and resonance energies. The bond energy is defined as the heat evolved at zero pressure and 298.16°K when two atoms form a chemical bond. The resonance energy is an empirical quantity defined in such a way that the sum of the bond energies and resonance energies can be used to calculate the standard heats of formation for a selected series of chemical compounds which exhibit resonance.

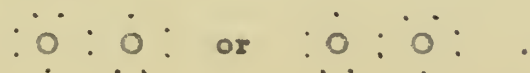
Pauling⁽¹⁾ first published a compilation of bond and resonance energies. The concept of bond energies has been refined recently and a comprehensive review of the experimental and theoretical studies up to the year 1950 has been given by Swarc.⁽²⁾ The discussion of bond energies given in this paper is based upon the latest available data. There has not been general agreement on some of the listed values. For example, the numerical values of the heat of sublimation of carbon and the bond energy of the nitrogen to nitrogen bond are controversial. The values for the former range from 125 Kcals/mole to 171.7 Kcals/mole, with different methods of experimentation giving different values. In order to supplement Pauling's well known tables of bond and resonance energies, calculations have been carried out to obtain tables using for the heat of sublimation of carbon both 135.8 Kcals/mole and 171.7 Kcals/mole.

It must be emphasized that the following discussion and data involve an oversimplification of the problem of bond energies and of their use in calculating heats of formation. In spite of this admittedly oversimplified approach to the calculation of heats of formation, the results are of considerable practical utility to the rocket engineer in estimating heats of formation and predicting rocket performance. The fact that even highly approximate estimates of heats of formation may be useful for estimating propellant performance is simply the result of very high heats of combustion for most propellants. The heats of formation of unknown propellants occur in propellant performance calculations as additive terms to the large heats of formation of compounds such as H_2O and CO_2 , which are known accurately. Hence considerable error can be tolerated in the theoretical estimates of heats of formation of propellants; and, therefore, even highly approximate calculations of heats of formation, based on tables of bond and resonance energies, are useful.

II. PRELIMINARY REMARKS

The bond energy of a single, double, or triple bond in an ideal diatomic molecule is numerically equal to the energy required to dissociate the molecule into atoms. The bond energies must be used with discretion and care must be taken to apply them only to

compounds which are known to have bonds of the type used. For example, the two oxygen atoms in O_2 are believed to be⁽¹⁾ connected by a single covalent and by two three-electron bonds so that its structure is largely



Hence it follows that the dissociation energy of O_2 should be much larger than the energy of a single covalent O-O bond as listed in the table.

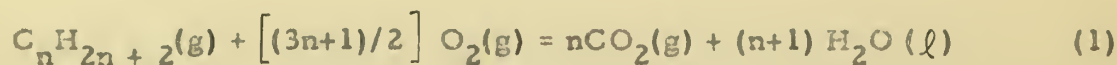
Individual bond energies for the polyatomic molecules are not available because the experimental measurements on the total heat of dissociation yield the sum of all the bond energies in the molecule. Hence it is necessary to calculate bond energies from experimental results on these molecules by indirect methods. In polyatomic molecules, in particular for organic compounds, relatively few different types of bonds are present. It has been suggested that each bond possesses an energy which is independent of the other bonds in the molecule, and that the heat of formation of the molecule from gaseous atoms is equal to the sum of the energies of the various bonds occurring in the molecule. This is the additivity principle that will be used throughout the following computations and is a necessary condition for the construction of

a bond energy table. Where large differences exist between the heats of formation calculated in this manner, and the heat of formation known to be the true value from experimental determinations, an amount of energy, designated as the resonance energy, must be added. Further discussion of the resonance energy will be given in Section V.

III. CALCULATIONS OF BOND ENERGIES INVOLVING CARBON

In the following discussions, the bond energy of the bond A-B will be symbolized by $D(A-B)$. The state of a chemical compound is identified by (g) for gaseous, (l) for liquid, and (c) for crystalline compounds; for carbon, in the form of graphite, the symbol (gr) will be used. Heat evolved in a reaction has a negative sign, and heat absorbed a positive sign.

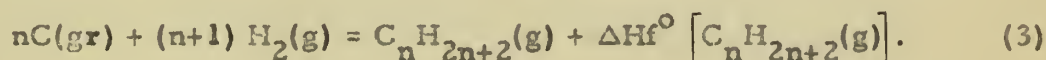
The heat of formation of a compound from gaseous atoms will be designated by ξ . For methane, according to the additivity rule, ξ is equal to the energy of four C-H bonds, $4D(C-H)$; for ethane, ξ equals the sum of the bond energies $D(C-C) + 6D(C-H)$. For the normal saturated hydrocarbons, C_nH_{2n+2} , we may form a general expression for the calculation of ξ by using the accurately known data on heat of combustion at constant pressure, ^(3,4) which will be designated by Q . For the process



the heat of reaction at constant pressure, Q , is related to the standard heats of formation, ΔH_f° , by the relation

$$Q = n\Delta H_f^\circ [CO_2(g)] + (n+1) \Delta H_f^\circ [H_2O(l)] - \Delta H_f^\circ [C_n H_{2n+2}(g)]. \quad (2)$$

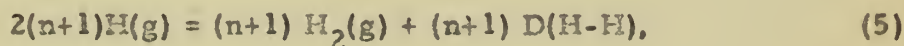
From the definition of $\Delta H_f^\circ [C_n H_{2n+2}(g)]$, it follows that



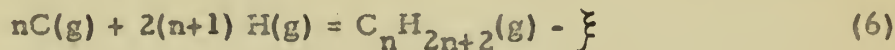
Using the additional relations

$$nC(g) = nC(gr) - nL(C) \quad (4)$$

and



where $L(C)$ is the heat absorbed during sublimation of one mole of carbon, it is seen upon summation of Eqs. (3), (4), and (5) that



where

$$\xi = \Delta H_f^\circ [C_n H_{2n+2}(g)] - nL(C) + (n+1) D(H-H). \quad (7)$$

The solution of ξ in terms of the heat of combustion is now obtained by combining Eq. (7) with Eq. (3), so that

$$\xi = -Q + n\Delta H_f^\circ [CO_2(g)] + (n+1)\Delta H_f^\circ [H_2O(l)] - nL(C) + (n+1)D(H-H). \quad (8)$$

By calculating ξ , the bond energies for the C-C and C-H bonds can be found since, by the additivity principle,

$$\xi = (n-1) D(C-C) + (2n+2) D(C-H). \quad (9)$$

Carrying the analysis a step further, Syrkin and Dyatkina⁽⁵⁾ found that the additivity principle cannot be used with accuracy for the first four members of the alkanes. However, all higher members conform to the additivity principle. The calculations of $D(C-C)$ and $D(C-H)$ have been carried out for the compounds $C_n H_{2n+2}$ with n varying from 5 to 12 (Cf. Appendix I).

By the use of a similar procedure we can calculate $D(C=C)$ from the heat of combustion data for the alkenes with the general formula $C_n H_{2n}$. Proceeding as before, the heat of formation of $C_n H_{2n}$ from the gaseous atoms, ξ , is

$$\xi = -Q + n\Delta H_f^\circ [CO_2(g)] + n\Delta H_f^\circ [H_2O(l)] + nD(H-H) - nL(C). \quad (10)$$

Using the additivity equation and the value of ξ obtained from Eq. (10), it is found that

$$D(C=C) = \xi - (n-2) D(C-C) - 2n D(C-H) \quad (11)$$

from which the C=C bond energy can be calculated. The values determined from the compounds C_5H_{10} to $C_{12}H_{24}$ were averaged in order to obtain the value listed in Table I.

The $C \equiv C$ bond energy was also calculated by this procedure. The additivity equation for the alkynes is

$$D(C \equiv C) = \xi - (n-2) D(C-C) + 2(n-1) D(C-H) \quad (12)$$

where it can easily be shown that

$$\xi = -Q + n\Delta H_f^\circ [CO_2(g)] + (n-1) \Delta H_f^\circ [H_2O(l)] - nL(C) + (n-1) D(H-H). \quad (13)$$

The values determined from the compounds C_5H_8 to $C_{12}H_{22}$ were again averaged to obtain the value listed in Table I.

The energies for the bonds between carbon and the halogens, C-F, C-Cl, C-Br, and C-I, were calculated by use of the heat of formation data of Rossini⁽⁶⁾ for the compounds CF_4 , CCl_4 , CBr_4 , and CH_3I respectively. The C-N bond energy was calculated from the heat of formation data for several amines, and the C-O bond energy from dimethyl ether. The energy for the C=O bond was

calculated from formaldehyde, the higher aldehydes, and the ketones. All three values have been listed in Table I. The $C \equiv N$ bond energy was obtained by averaging results of the bond energy computations for HCN , CH_3CN , and C_6H_5CN . The $C-S$ bond energy was obtained by utilizing the known heat of formation of dimethyl sulfide.

IV. CHEMICAL BONDS NOT INVOLVING CARBON

The energies for the bonds involving the halogens were obtained from spectroscopic data.[†] Some of the references consulted listed the bond energies $D(A-B)$ for the bond $A-B$ at a temperature of $0^\circ K$. For these values, an appropriate temperature correction to $298.16^\circ K$ has been carried out. If $D(A-B)^0$ is the bond energy at $0^\circ K$, then⁽⁷⁾

$$D(A-B) = D(A-B)^0 + \Delta (5/2)RT + \Delta RT^2 (d \ln Q_{vib} / dT) \quad (12)$$

where Q_{vib} is the vibrational partition function. For ideal gaseous diatomic molecules, such as HF , it is known that

$$RT^2 [d(\ln Q_{vib}) / dT] = RT [\exp(u) - 1]^{-1} u \quad (13)$$

[†] References used for these calculations are listed in Table II.

where $u = hc\omega^*/kT$; h = Planck's constant; c = velocity of light; ω^* = wave number corresponding to the (forbidden) transition from the vibrational ground level to the first excited vibrational level, in each case the rotationless state being involved; and k = Boltzmann constant. Values for u or ω^* are given in the literature.⁽⁸⁾ Details concerning the calculations for several special cases are given in Appendix II.

The bond energies listed are always dependent upon the products formed as the result of dissociation. Where ambiguity exists regarding the products of dissociation, multiple entries are given in Table II.

Through use of the data listed by Rossini,⁽⁶⁾ the energies for other bonds can be obtained. Following the methods outlined by Pauling,⁽⁶⁾ the energies of the bonds Si-Si and Ge-Ge are one-half of the heats of sublimation of the crystals of these elements. These crystals have the diamond arrangement, with each atom connected by single bonds to its four nearest neighbors, which surround it tetrahedrally. The values for the P-P and As-As bond energies are one-sixth of the heat evolved when the molecules $P_4(g)$ and $As_4(g)$ are formed from gaseous atoms. Both of these compounds have tetrahedral crystals with six bonds along the tetrahedron edges. The energy for the S-S bond is one-eighth of the heat of formation of $S_8(g)$ from the gaseous atoms, since the S_8 molecule

is an eight-membered ring containing eight S-S bonds.

The value for the N-H and N-N bond energies were selected from the work of Cole and Gilbert.⁽⁹⁾ Some controversy still exists with respect to the N-H bond energy; however, the value of 88.0 Kcals was favored by Cole and Gilbert after various theoretical studies, including a study of bond lengths. The value for the N-N bond energy then was calculated using the known heat of formation of the molecule hydrazine (N_2H_4).

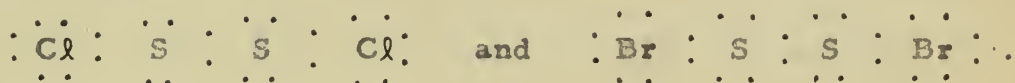
Again following the methods described by Pauling, the O-H bond energy has been calculated from the value of ΔHf° for $\text{H}_2\text{O}(\text{g})$, after which the O-O bond energy was found using the value of ΔHf° for hydrogen peroxide.

The bond energies involving silicon and the atoms H, F, Cl, O, Br, and S were computed from the heat of formation data of Rossini⁽⁶⁾ for the molecules SiH_4 , SiF_4 , SiCl_4 , SiO_4 , SiBr_4 , and SiS_2 . The heats of formation available for SiO_2 and SiS_2 referred to the compounds in the crystalline state, which have four bonds per molecule. These crystals are giant polymers, each silicon atom being connected by single bonds to four oxygen or sulfur atoms, each of which is in turn bonded to two silicon atoms.

The bond energies for P-H, P-Cl, and P-Br were computed from the standard heat of formation of PH_3 , PCl_3 , and PBr_3 respectively, making use of the heat of sublimation of phosphorus.

The bond energies As-H, As-F, As-Cl, and As-Br were found using the standard heats of formation for the molecules AsH₃, AsF₃, AsCl₃, and AsBr₃, and the heat of sublimation of As, since the standard state for As is crystalline.

The energies for the S-Cl and S-Br bonds were found from heats of formation of S₂Cl₂ and S₂Br₂, respectively. For the present calculations, the structures for these two molecules were assumed to be



Since Rossini's⁽⁶⁾ heat of formation for S₂Br₂ referred to the liquid state and the heat of vaporization was not available in the literature, Trouton's rule was used for estimating this quantity as a necessary step in the calculation of the S-Br bond energy. The error involved in this approximation is small.

The S-H bond energy was obtained through use of the heat of formation for H₂S and the heat of sublimation of crystalline sulfur.

The bond energies for N-F, F-O, and Cl-O were obtained using the heats of formation for NF₃, F₂O, and Cl₂O, respectively.

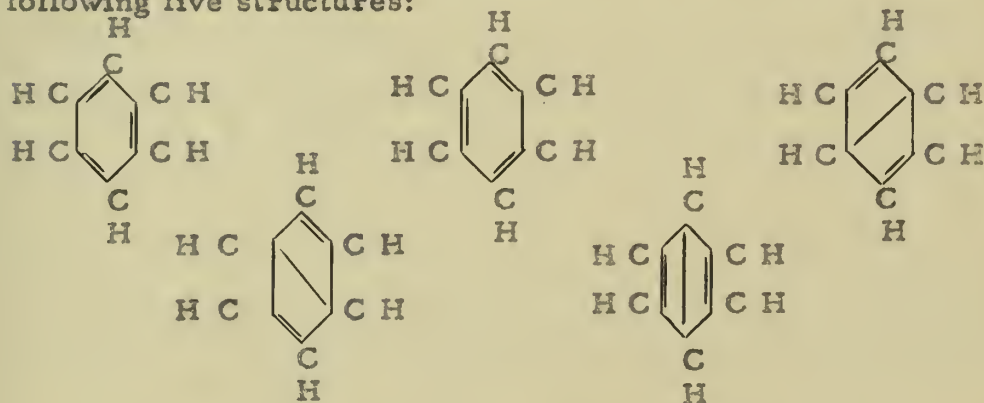
The energy of the N≡N bond has been the subject of much

controversy. Estimates range from 172 Kcals to 272 Kcals. (1, 10, 11)
The value of 225.5 Kcals, preferred by Gaydon and others, has been selected.

V. RESONANCE ENERGY CALCULATIONS

If the bond energies listed in Table I and II are used to estimate the standard heats of formation, erroneous results may be obtained because no provision has been made for the inclusion of extra energy associated with resonance.* The resonance energy may make an appreciable contribution to the heat of formation of some chemical compounds.

The effect of resonance can be seen readily by considering the benzene molecule. This molecule can resonate between the following five structures:



Because of stabilization of the benzene molecule by resonance, the

* It should be noted that the method of calculations described in this section does not depend on the physical "reality" of the resonance concept, which is used essentially as an empirical interpolation device.

heat of formation from gaseous atoms will be considerably greater than the heat of formation computed as the sum of $3D(C-C) + 3D(C=C) + 6D(C-H)$. Denoting the resonance energy by ξ_R , the expression for the heat of formation from the gaseous atoms can be written

$$\xi = 3D(C-C) + 3D(C=C) + 6D(C-H) + \xi_R. \quad (14)$$

In general, resonance energies are computed as the difference between the experimentally determined heats of formation, and the heats of formation calculated by taking the sum of the energies for the separate chemical bonds.*

The standard heats of formation were obtained either from Rossini,⁽⁶⁾ or from the conversion of heats of combustion data. Much of the data on heats of combustion was only available for compounds in either the crystalline or liquid states. This necessitated the use of heats of fusion and heats of vaporization,

* Objections have been raised recently against the concept of resonance energies as being the difference in energy between the actual resonating molecule and a hypothetical molecule made out of "normal" bonds. For a recent discussion concerning the calculation of compressional energy, bond hybridization corrections, and resonance energy, reference should be made, for example, to a paper by C. A. Coulson and S. L. Altman, *Trans. Faraday Soc.*, 48, April (1952), pp. 293-302. It should be noted, however, that for the practical applications with which this paper is concerned, the conventional notion of resonance energy is entirely adequate.

which also were not always available. Therefore, where necessary, estimates were made using the aforementioned Trouton's Rule, and also the relation

$$\frac{\Delta H_{\text{fusion}}}{T_{\text{melt. pt.}}} \approx 10 \quad (15)$$

For molecules with a C=O bond, the choice of the energy value to use for this bond is dependent upon the structure of the entire compound. Thus, the dialkyl carbonates have a structure similar to the ketones with respect to the C=O bond and therefore, the $D(\text{C=O})$ of Table I, computed from ketones, was used. For furfural, however, the $D(\text{C=O})$ computed from the higher aldehydes was used. In order to estimate the resonance energy for carbon monoxide and carbon dioxide, the $D(\text{C=O})$ of Table I, computed from formaldehyde, was used.

The resonance energy computations are given in Appendix III, and the results comprise Table III. Pauling's corresponding resonance energies are also listed in Table III for comparison.

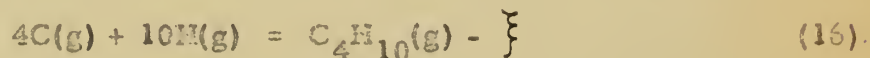
VI. USE OF TABLES OF BOND AND RESONANCE ENERGIES FOR ESTIMATING STANDARD HEATS OF FORMATION

Application of the tables of bond and resonance energies will now be shown by several examples. The first few calculations of

standard heats of formation are routine applications of the listed data. However, for several propellants having the nitro group as part of their molecular structure, indirect procedures of calculation are necessary because it is not possible to predict the influence of the nitro group on the total resonance energy of the molecule.

(a) n-Butane

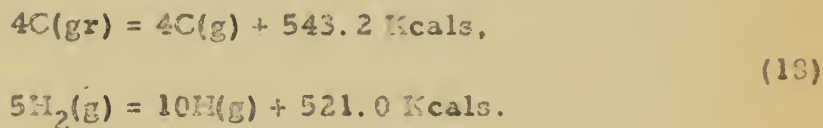
By definition of the heat of formation of a compound from the gaseous atoms, ξ , it can be written



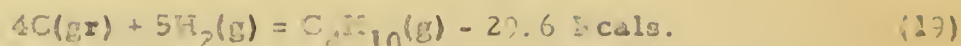
where

$$\xi = 3D(C-C) + 10D(C-H). \quad (17)$$

Using the bond energies consistent with a heat of sublimation for carbon of 135.8 Kcals, it is found that $\xi = 1093.8$ Kcals. To form the equation for the formation of n-butane from the elements in their respective standard states, use is made of the additional relations



Addition of Eqs. (16) and (18) obtains



Thus through the use of the bond energy tables, the standard heat of formation for n-butane has been found to be $\Delta H_f^\circ = -29.6 \text{ Kcals.}$ Rossini⁽⁶⁾ lists the value $\Delta H_f^\circ = -29.8 \text{ Kcals.}$ which agrees closely with the calculated value.

(b) Methyl Alcohol

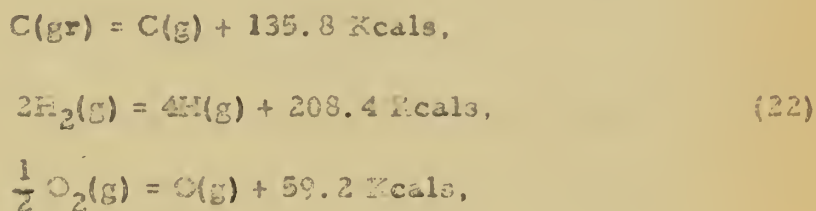
The relation for the formation of the compound from the separated atoms is



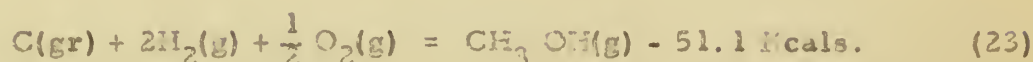
where

$$\xi = D(C-O) + 3D(C-H) + D(O-H). \quad (21)$$

Again using the bond energies consistent with $L(C) = 135.8 \text{ Kcals.}$ it is found that $\xi = 454.5 \text{ Kcals.}$ Adding Eq. (20) to the sum of the following



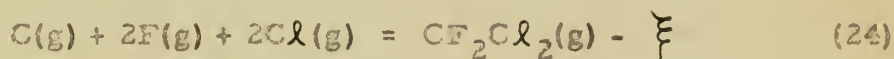
The equation for the standard heat of formation is obtained, viz.,



This computed value of ΔHf° agrees reasonably well with Rossini's value of - 48.10 Kcals.

(c) Difluoro-Dichloro-Methane

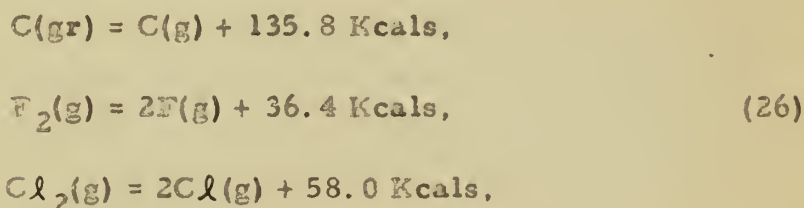
The equation for the formation of this compound from the gaseous atoms is



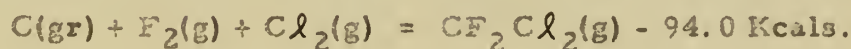
where

$$\mathfrak{F} = 2\text{D}(\text{C}-\text{F}) + 2\text{D}(\text{C}-\text{Cl}). \quad (25)$$

Solving for \mathfrak{F} by using bond energies consistent with $\text{L}(\text{C}) = 135.8 \text{ Kcals.}$ we find $\mathfrak{F} = 324.2 \text{ Kcals.}$ Adding Eq. (24) to the following



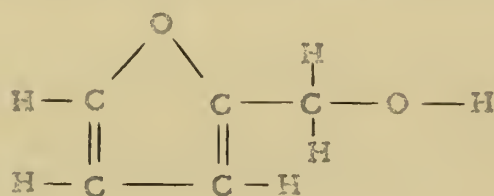
the equation for the standard heat of formation is obtained, viz.,



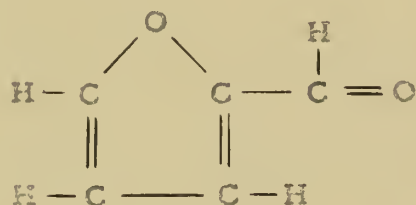
The standard heat of formation of CF_2Cl_2 does not appear to have been determined experimentally.

(d) Furfuryl Alcohol

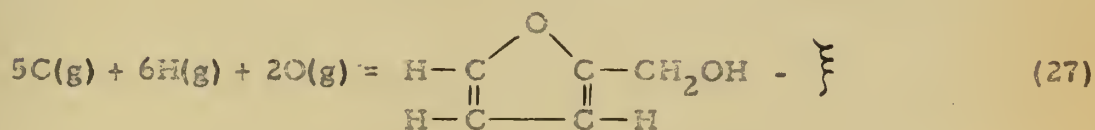
The calculation of ΔH_f° for this compound requires inclusion of an appropriate estimate for the resonance energy. This compound has predominantly the following structure



By reference to Table III, it is seen that this structure is similar to furfural, viz.,



which has a resonance energy of 30.1 Kcals/mole consistent with $L(\text{C}) = 135.8$ Kcals. Assuming that the resonance energy of furfuryl alcohol is also 30.1 Kcals/mole,



where

$$\xi = 3D(C-O) + 2D(C=C) + 2D(C-C) + 5D(C-H) + D(O-H) + 30.12 \text{ Kcals.} \quad (28)$$

Using the data from Tables I and II, it is found that $\xi = 1165.4 \text{ Kcals.}$

With the additional relations

$$5C(\text{gr}) = 5C(\text{g}) + 679.0 \text{ Kcals,}$$

$$3H_2(\text{g}) = 6H(\text{g}) + 312.6 \text{ Kcals,} \quad (29)$$

$$O_2(\text{g}) = 2O(\text{g}) + 118.3 \text{ Kcals,}$$

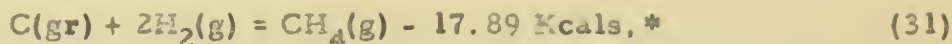
it is found upon addition that $\Delta H_f^0 = -55.5 \text{ Kcals.}$ Experimental data are not available for comparison with this calculated value.

(e) Tetranitromethane

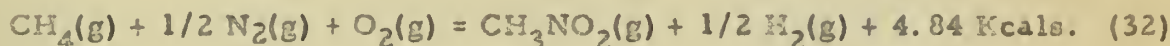
The propellants containing the nitro group as part of their molecular structure are very important to the rocket engineer. In order to estimate the heat of formation of these propellants, an indirect procedure is used as follows. Rossini⁽⁶⁾ lists for $CH_3NO_2(l)$ the value $\Delta H_f^0 = -21.23 \text{ Kcals/mole.}$ The heat of vaporization of CH_3NO_2 is $8.23 \text{ Kcal/mole,}^{(4)}$ and therefore,

$$C(\text{gr}) + 3/2 H_2(\text{g}) + 1/2 N_2(\text{g}) + O_2(\text{g}) = CH_3NO_2(\text{g}) - 13.0 \text{ Kcals.} \quad (30)$$

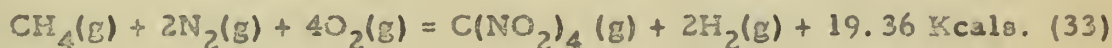
Also



so that upon subtraction of Eq. (31) from Eq. (30) it is found that



Equation (32) may be interpreted as giving the energy absorbed when an atom of hydrogen is replaced by a nitro group in methane. Applying this to tetranitromethane, which has four such substitutions, it can be written



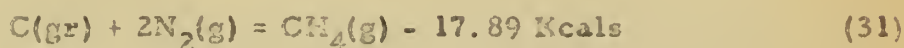
The addition of Eqs. (32) and (33) yields $\Delta\text{Hf}^\circ[\text{C}(\text{NO}_2)_4(\text{g})] = 1.47 \text{ Kcals.}$ However, the experimentally determined ΔHf° for this compound is 18.0 Kcals. (6, 4) Therefore, this calculation is not adequate; it appears that interference between the NO_2 groups makes tetranitromethane less stable than expected.

(f) Hexanitromethane

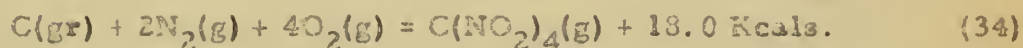
Applying the same procedure in estimating ΔHf° for this compound, i. e., replacing the six hydrogen atoms in C_2H_6 by NO_2

* This value is listed by Rossini (Reference 6). It does not agree with the value calculated from tables of bond energies since the additivity rule does not apply to this hydrocarbon.

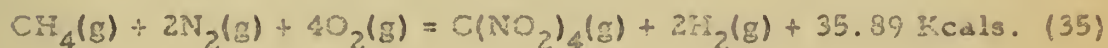
and absorbing 6(4.84) Kcals in the process, it is found that $\Delta H_f^\circ [C_2(NO_2)_6(g)] = + 8.80$ Kcals. The compound is evidently less stable and will therefore have a heat of formation more positive than the above value. A much more accurate estimate will be obtained from the equations



and



Subtraction of Eq. (31) from Eq. (34) leads to the result



Thus, $1/4 (35.89) = 8.97$ Kcals is now found as the energy absorbed in replacing an H atom by NO_2 , taking account of the interference of the NO_2 groups in tetranitromethane. Thus, for hexanitroethane with six substitutions of the H atom by NO_2 , it can be written



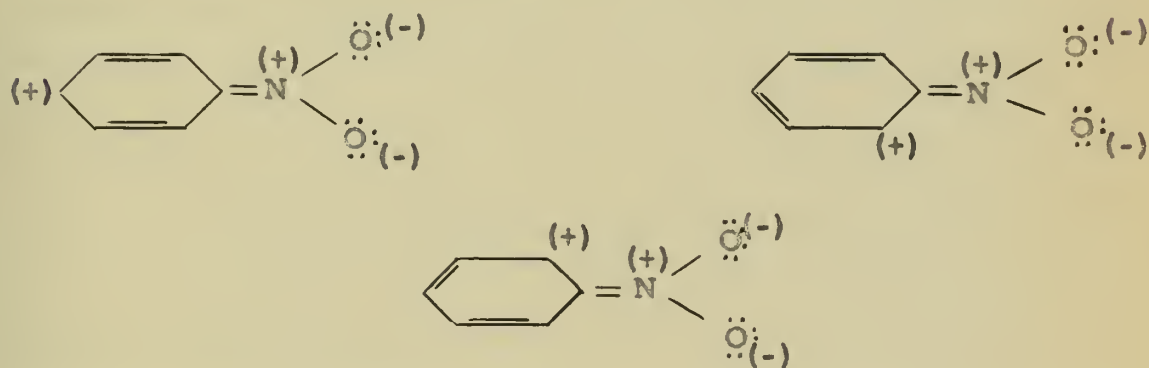
Using the value of ΔH_f° for $C_2H_6(g)$ listed by Rossini (-20.25 Kcals),

it is found that $\Delta H_f^\circ [C_2(NO_2)_6(g)] = + 33.6 \text{ Kcals}$. Upon estimating the sum of the heats of vaporization and fusion to be approximately 10 Kcals, it can be seen that

$$\Delta H_f^\circ [C_2(NO_2)_6(c)] \approx + 23 \text{ Kcals/mole.} \quad (37)$$

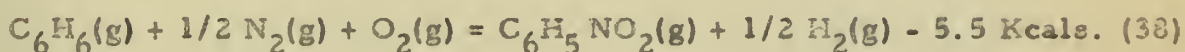
(g) Dinitrobenzene

Pauling⁽¹⁾ explains that whenever the group R, replacing an H atom in benzene to form C_6H_5R , contains an electronegative atom and a double or triple bond conjugated to the benzene ring, additional resonance energy is present. Thus, for the NO_2 group replacing an H atom in benzene, resonance will occur not only between the normal benzene structures as shown previously, but also between the following structures:

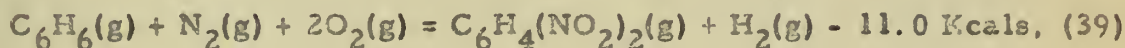


wherein the nitro group accepts a pair of electrons from the benzene ring. Using the amount of heat absorbed in the replacement of the

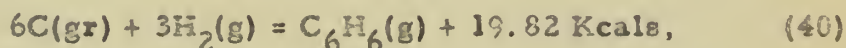
hydrogen atom in methane by a nitro group, namely 4.84 Kcals, the standard heat of formation of nitrobenzene is calculated to be 24.7 Kcals. However, due to the above resonance, it would be expected that the true value is less positive, i. e., nitrobenzene should be more stable. Rossini⁽⁶⁾ lists $\Delta H_f^\circ [C_6H_5NO_2(g)] = + 14.27$ Kcals/mole. Therefore, for this substitution of NO_2 on the benzene ring, the appropriate equation is



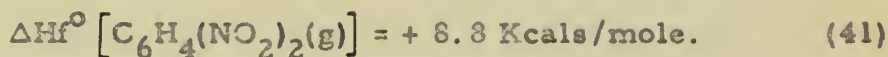
since $\Delta H_f^\circ [C_6H_6(g)] = + 19.82$ Kcals/mole. Upon applying this value of Eq. (38) in the calculation of ΔH_f° for dinitrobenzene, it is seen that



and, since



it is found by addition that



One would expect that the true value of ΔH_f° for dinitrobenzene is somewhat less positive than 8.8 Kcals/mole because of the possibility of additional resonance stabilization resulting from the introduction of two NO_2 -groups into the benzene ring.

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Table I. Energies for Bonds Involving Carbon*

	$L(C) = 135.8 \text{ kcal/s}^{(12)}$	$L(C) = 171.7 \text{ kcal/s}^{(6)}$
1. D(C-C)	67.6	85.5
2. D(C-H)	89.1	98.1
3. D(C=C)	107.1	143.0
4. D(C \equiv C)	143.0	194.3
5. D(C-Cl)	69.3	78.3
6. D(C-Br)	57.8	66.8
7. D(C-I)	55.3	64.2
8. D(C-F)	92.8	101.7
9. D(C-N)	72.1	81.0
10. D(C-O)	76.6	85.4
11. D(C-S)	54.9	63.7
12. D(C=O)	148.7	166.6
	153.9 [†]	171.8 [†]
	165.3 ^{††}	183.2 ^{††}
13. D(C \equiv N)	183.7	210.6

* All bond energies are in kcal/s/mole.

** Determined from formaldehyde.

† Determined from higher aldehydes.

†† Determined from Ketones.

Table II. Energies for Bonds not Involving Carbon

1.	$D(F-F) = 36.4^{(13)}$
2.	$D(Br-Br) = 46.4^{(8)}$
3.	$D(Cl-Cl) = 58.0^{(6)}$
4.	$D(I-I) = 36.5^{(8)}$
5.	$D(H-H) = 104.2^{(6)}$
6.	$D(H-F) = 134.5^{(14)}$
7.	$D(Br-F) = 50.7 \text{ or } 60.8^{(15)*}$
8.	$D(I-F) = 46.5 \text{ or } 67.0^{(15)†}$
9.	$D(I-Br) = 42.5^{(15)}$
10.	$D(Cl-F) = 59.9 \text{ or } 61.2^{(15)‡}$
11.	$D(Br-Cl) = 52.2^{(15)}$
12.	$D(I-Cl) = 50.3^{(15)}$
13.	$D(H-Cl) = 103.2$
14.	$D(H-Br) = 87.6$
15.	$D(H-I) = 71.6$
16.	$D(N-N) = 60.0^{(2)(9)}$
17.	$D(N-H) = 88.0^{(9)}$
18.	$D(N\equiv N) = 225.5^{(10)}$
19.	$D(Si-Si) = 44.0$
20.	$D(Ge-Ge) = 39.2$

* The first value refers to the Br atom in the excited state and the F atom in the normal state; the second value refers to the F atom in the excited state and the Br atom in the normal state.

† The first value refers to the I atom in the excited state and the F atom in the normal state; the second value refers to the F atom in the excited state and the I atom in the normal state

‡ The first value refers to the Cl atom in the normal state and the F atom in the excited state; the second value refers to the F atom in the normal state and the Cl atom in the excited state.



Table II. (Continued)

- 21. $D(\text{As-As}) = 34.5$
 - 22. $D(\text{P-P}) = 47.9$
 - 23. $D(\text{S-S}) = 50.3$
 - 24. $D(\text{O-O}) = 33.1$
 - 25. $D(\text{O-H}) = 110.6$
 - 26. $D(\text{Si-H}) = 77.8$
 - 27. $D(\text{Si-F}) = 132.7$
 - 28. $D(\text{Si-Cl}) = 87.4$
 - 29. $D(\text{Si-O}) = 102.9$
 - 30. $D(\text{Si-Br}) = 70.4$
 - 31. $D(\text{Si-S}) = 57.3$
 - 32. $D(\text{O} \equiv \text{O}) = 118.3^{(6)}$
 - 33. $D(\text{H-P}) = 76.4$
 - 34. $D(\text{H-As}) = 58.6$
 - 35. $D(\text{H-S}) = 81.1$
 - 36. $D(\text{N-F}) = 64.9$
 - 37. $D(\text{P-Cl}) = 78.5$
 - 38. $D(\text{P-Br}) = 63.9$
 - 39. $D(\text{As-F}) = 111.2$
 - 40. $D(\text{As-Cl}) = 73.2$
 - 41. $D(\text{As-Br}) = 58.4$
 - 42. $D(\text{S-Cl}) = 60.0$
 - 43. $D(\text{S-Br}) = 53.4$
 - 44. $D(\text{F-O}) = 45.0$
 - 45. $D(\text{Cl-O}) = 49.5$
-



Table III. Resonance Energies

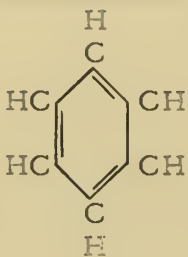
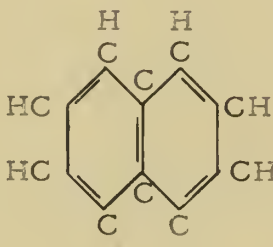
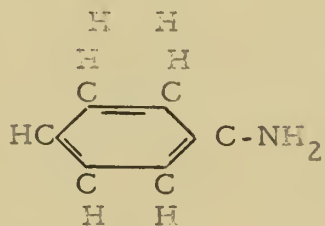
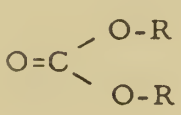
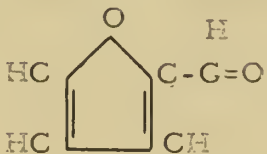
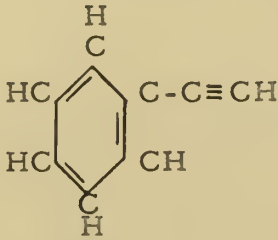
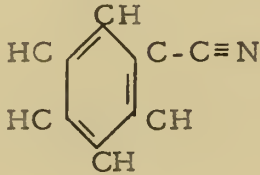
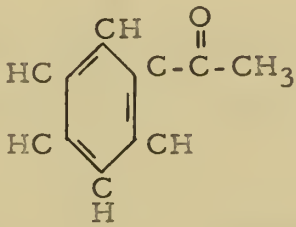
Substance	Reference Structure	Resonance Energy (kcal)	Pauling's Values (kcal)
Benzene C_6H_6		48.9	39
Naphthalene $C_{14}H_{10}$		88.0	75
Aniline $C_6H_5NH_2$		69.6	45
Dialkyl carbonates R_2CO_3		32.7	42
Furfural C_4H_3OCHO		30.1	-



Table III. (Continued)

Substance	Reference Structure	Resonance Energy (kcal)	Pauling's Values (kcal)
Phenyl acetylene C_6H_5CCH		55.5	49
Phenyl cyanide $C_6H_5-COCH_3$		57.0	44
Acetophenone $C_6H_5-COCH_3$		49.0	46
Carbon Monoxide CO	$C=O$	90.7*	72.7
Carbon Dioxide CO ₂	$O=C=O$	50.7	33



APPENDIX I

SUMMARY OF CALCULATIONS USED TO DETERMINE BOND ENERGIES INVOLVING CARBON [†]

1. Calculation of D(C-C) and D(C-H)

From the main body of this thesis

$$\begin{aligned} \xi = & - Q + n\Delta H_f^\circ [\text{CO}_2(\text{g})] + (n+1)\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] \\ & - nL(\text{C}) + (n+1) D(\text{H-H}), \end{aligned} \quad (8)$$

and

$$\xi = (n - 1) D(\text{C-C}) + (2n+2) D(\text{C-H}). \quad (9)$$

Results obtained by use of Eq. (8) for the alkanes from pentane to dodecane are listed in Table (A-I).

Table A-I. Data Used for Computation of ξ .

Compound	- Q	$-n\Delta H_f^\circ$ CO ₂ (g)	$-(n+1)\Delta H_f^\circ$ H ₂ O(l)	$nL(\text{C})^*$	$nL(\text{C})$	$-(n+1)$ D(H-H)	$-\xi^*$	$-\xi$
C ₅ H ₁₂	845.3	470.5	409.8	858.5	679.0	625.2	1518.7	1339.2
C ₆ H ₁₄	1001.6	564.6	478.1	1030.2	814.8	729.4	1800.7	1585.3
C ₇ H ₁₆	1158.2	658.7	546.4	1201.9	950.6	833.6	2082.4	1831.1

[†] The bond energies consistent with $L(\text{C}) = 171.7$ Kcals are starred(*).



Table A-I. Continued

Compound	- Q	$-n\Delta H_f^\circ$ CO ₂ (g)	$-(n+1)\Delta H_f^\circ$ H ₂ O(l)	$nL(C)^*$	$nL(C)$	$-(n+1)$ D(H-H)	$-\xi^*$	$-\xi$
C ₈ H ₁₈	1314.6	752.8	614.7	1373.6	1086.4	937.8	2364.3	2077.1
C ₉ H ₂₀	1471.3	846.9	683.0	1545.3	1222.2	1042.0	2645.9	2322.8
C ₁₀ H ₂₂	1628.2	941.0	751.3	1717.0	1358.0	1146.2	2927.3	2568.3
C ₁₁ H ₂₄	1784.4	1035.0	819.6	1888.7	1493.8	1250.4	3209.4	2814.5
C ₁₂ H ₂₆	1941.9	1129.2	887.9	2060.4	1629.6	1354.6	3490.2	3059.4

Two equations in the two unknowns, D(C-C) and D(C-H), may be formed through use of Eq. (9) as follows:

$$4D(C-C) + 12D(C-H) = 1518.7^* \text{ or } 1339.2$$

$$5D(C-C) + 14D(C-H) = 1800.7^* \text{ or } 1585.3$$

$$6D(C-C) + 16D(C-H) = 2082.4^* \text{ or } 1831.1$$

$$7D(C-C) + 18D(C-H) = 2364.3^* \text{ or } 2077.1$$

By summation

$$22D(C-C) + 60D(C-H) = [7766.1^* \text{ or } 6832.9] \text{ Kcals.}$$

$$8D(C-C) + 20D(C-H) = 2645.9^* \text{ or } 2322.8$$

$$9D(C-C) + 22D(C-H) = 2927.3^* \text{ or } 2568.3$$

$$10D(C-C) + 24D(C-H) = 3209.4^* \text{ or } 2814.5$$

$$11D(C-C) + 26D(C-H) = 3490.2^* \text{ or } 3059.4$$

By summation

$$38D(C-C) + 92D(C-H) = [12,272.8^* \text{ or } 10,765.0] \text{ Kcals.}$$



Solving the preceding equations, it is found that

$$D(C-H)^* = 98.1 \text{ Kcals}$$

$$D(C-C)^* = 85.5 \text{ Kcals}$$

$$D(C-H) = 89.1 \text{ Kcals}$$

$$D(C-C) = 67.6 \text{ Kcals.}$$

2. Calculation of D(C=C)

This bond energy is obtained using, from the text,

$$\begin{aligned} \xi = & -Q + n\Delta H_f^\circ [CO_2(g)] + n\Delta H_f^\circ [H_2O(l)] \\ & + nD(H-H) - nL(C) \end{aligned} \quad (10)$$

and

$$D(C=C) = \xi - (n-2) D(C-C) - 2n D(C-H). \quad (11)$$

The solutions of Eq. (10) for the alkenes from pentene to dodecene are listed in Table(A-II).

Table (A-II). Data Used for Computation of

Compound	-Q	$-n\Delta H_f^\circ$ CO ₂ (g)	$-n\Delta H_f^\circ$ H ₂ O(l)	$-n$ D(H-H)	$nL(C)^*$	$nL(C)$	$-\xi^*$	$-\xi$
C ₅ H ₁₀	806.35	470.5	341.6	521.0	358.5	679.0	1384.7	1205.3
C ₆ H ₁₂	964.26	564.6	409.8	625.2	1030.2	814.8	1665.5	1450.1
C ₇ H ₁₄	1121.69	658.7	478.1	729.4	1201.9	950.6	1946.4	1695.1



Table (A-II). Continued

Compound	-Q	$-n\Delta H_f^\circ$ CO ₂ (g)	$-n\Delta H_f^\circ$ H ₂ O(l)	-n D(H-H)	nL(C)*	nL(C)	$-\xi^*$	$-\xi$
C ₈ H ₁₆	1279.13	752.8	546.4	833.6	1353.6	1086.4	2227.3	1940.1
C ₉ H ₁₈	1436.58	846.9	614.7	937.8	1545.3	1222.2	2508.1	2185.0
C ₁₀ H ₂₀	1594.02	941.0	683.0	1042.0	1717.0	1358.0	2789.0	2430.0
C ₁₁ H ₂₂	1751.46	1035.1	751.3	1146.2	1888.7	1493.8	3069.8	2674.9
C ₁₂ H ₂₄	1908.91	1129.2	819.6	1250.4	2060.4	1629.6	3340.7	2909.9

The values of D(C=C) are computed by using Eq. (11) for each of the compounds listed in Table (A-II). It is found by taking the average of the eight values thus obtained, that

$$D(C=C)^* = 143.0 \text{ Kcals}$$

$$D(C=C) = 107.1 \text{ Kcals.}$$

3. Calculation of D(C≡C)

This triple bond energy is obtained through use of the following equations

$$\begin{aligned} \xi = & -Q + n\Delta H_f^\circ [\text{CO}_2(\text{g})] + (n-1)\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] - nL(\text{C}) \\ & + (n-1) D(\text{H-H}) \end{aligned} \quad (12)$$





Table (A-IV). Data Used for Computation of the Bond Energy, $D(C\equiv C)$

Compound	$-(n-2)D(C-C)^*$	$-2(n-1)D(C-H)^*$	$-(n-2)D(C-C)$	$-2(n-1)D(C-H)$
C_5H_8	256.5	784.8	202.8	712.8
C_6H_{10}	342.0	981.0	270.4	891.0
C_7H_{12}	427.5	1177.2	338.0	1069.2
C_8H_{14}	513.0	1373.4	405.6	1247.4
C_9H_{16}	598.5	1569.6	473.2	1425.6
$C_{10}H_{18}$	684.0	1765.8	540.8	1603.8
$C_{11}H_{20}$	769.5	1962.0	608.4	1782.0
$C_{12}H_{22}$	855.0	2158.2	676.0	1960.2
Total	4446.0	11772.0	3515.2	10692.0

It is found by taking the sum of each of the columns of Table A-IV and of the ξ columns from Table A-III that

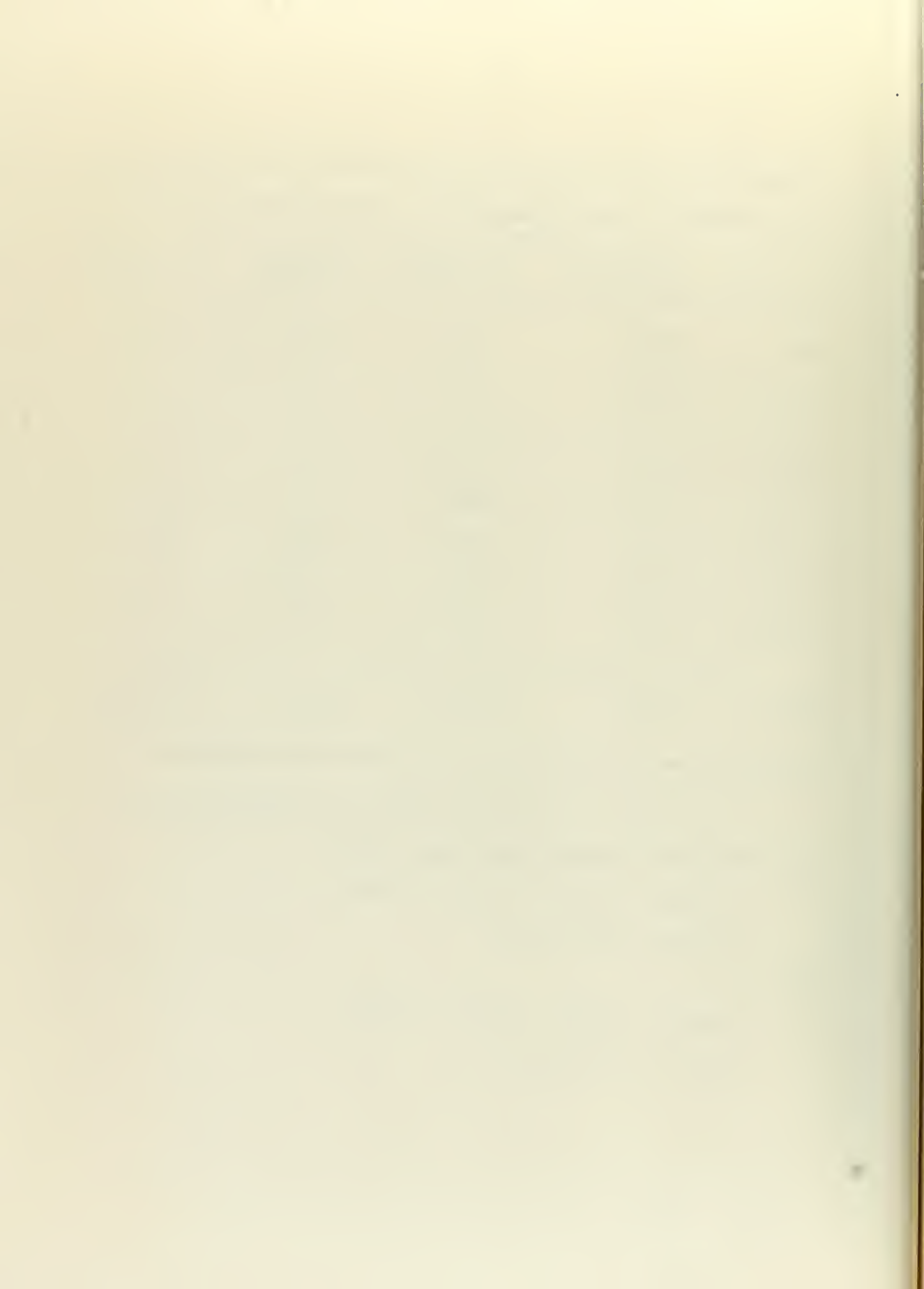
$$8D(C\equiv C)^* = 17772.0 - 4446.0 - 11772.0$$

$$D(C\equiv C)^* = 194.3 \text{ Kcals}^*$$

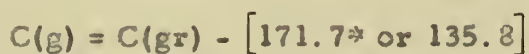
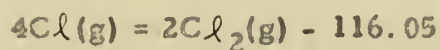
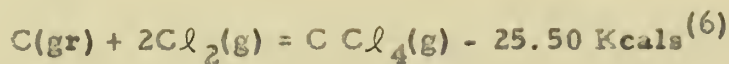
and

$$8D(C\equiv C) = 15350.8 - 3515.2 - 10692.0$$

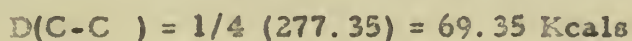
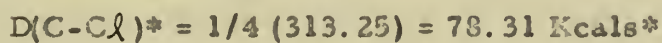
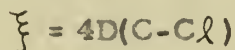
$$D(C\equiv C) = 143.0 \text{ Kcals.}$$



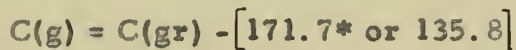
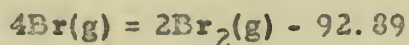
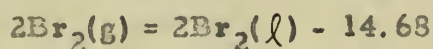
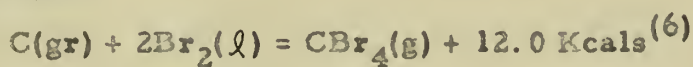
4. D(C-Cl)



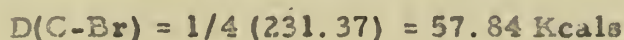
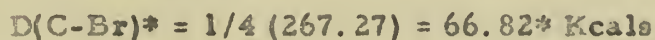
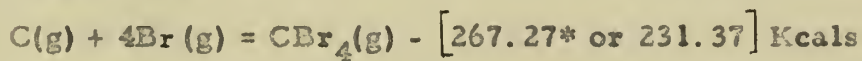
By addition



5. D(C-Br)

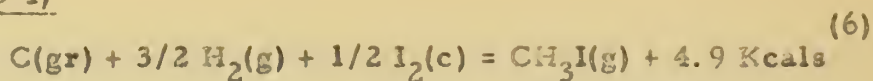


By addition





6. D(C-I)



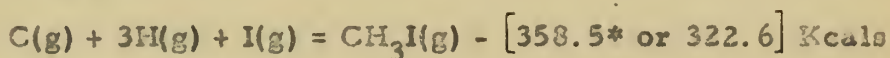
$$\text{C(g)} = \text{C(gr)} - [171.7* \text{ or } 135.8]$$

$$1/2 \text{I}_2(\text{g}) = 1/2 \text{I}_2(\text{c}) - 7.4$$

$$3\text{H}(\text{g}) = 3/2 \text{H}_2(\text{g}) - 156.3$$

$$\text{I(g)} = 1/2 \text{I}_2(\text{g}) - 18.3$$

By addition

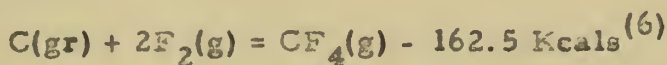


$$\} = 3\text{D(C-H)} + \text{D(C-I)}$$

$$\text{D(C-I)*} = 358.5 - 3(98.1) = 64.2* \text{ Kcals}$$

$$\text{D(C-I)} = 322.6 - 3(89.1) = 55.3 \text{ Kcals}$$

7. D(C-F)



$$4\text{F(g)} = 2\text{F}_2(\text{g}) - 72.78$$

$$\text{C(g)} = \text{C(gr)} - [171.7 \text{ or } 135.8]$$

By addition



$$\} = 4\text{D(C-F)}$$

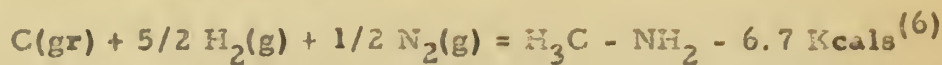
$$\text{D(C-F)*} = 1/4 (406.98) = 101.74 \text{ Kcals*}$$

$$\text{D(C-F)} = 1/4 (371.08) = 92.77 \text{ Kcals.}$$



8. D(C-N)

(a) From Methylamine



$$\text{C(g)} = \text{C(gr)} - [171.7^* \text{ or } 135.8]$$

$$5\text{H(g)} = 5/2 \text{H}_2(\text{g}) - 260.5$$

$$\text{N(g)} = 1/2 \text{N}_2(\text{g}) - 112.8$$

By addition

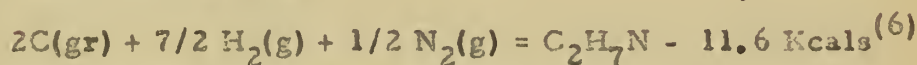
$$\text{C(g)} + 5\text{H(g)} + \text{N(g)} = \text{H}_3\text{C} - \text{NH}_2 - [551.7^* \text{ or } 515.8] \text{ Kcals}$$

$$\} = \text{D(C-N)} + 2\text{D(N-H)} + 3\text{D(C-H)}$$

$$\text{D(C-N)}^* = 551.7 - 176 - 294.3 = 81.4 \text{ Kcals}^*$$

$$\text{D(C-N)} = 515.8 - 176 - 267.3 = 72.5 \text{ Kcals.}$$

(b) From Ethylamine



$$2\text{C(g)} = 2\text{C(gr)} - [343.4^* \text{ or } 271.6]$$

$$7\text{H(g)} = 7/2 \text{H}_2(\text{g}) - 364.7$$

$$\text{N(g)} = 1/2 \text{N}_2(\text{g}) - 112.8$$

By addition

$$2\text{C(g)} + 7\text{H(g)} + \text{N(g)} = \text{C}_2\text{H}_7\text{N} - [832.5^* \text{ or } 760.7] \text{ Kcals}$$

$$\} = \text{D(C-C)} + \text{D(C-N)} + 2\text{D(N-H)} + 5\text{D(C-H)}$$

$$\text{D(C-N)}^* = 832.5 - 85.5 - 176 - 490.5 = 80.5 \text{ Kcals}^*$$

$$\text{D(C-N)} = 760.7 - 67.6 - 176 - 445.5 = 71.6 \text{ Kcals}$$

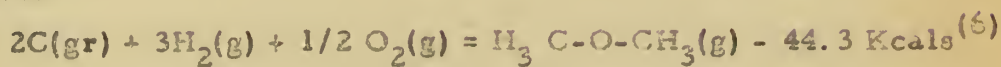


By taking the average of the previous two computations it is found that

$$D(C-N)^* = 81.0 \text{ Kcals}^*$$

$$D(C-N) = 72.1 \text{ Kcals}$$

9. D(C-O)

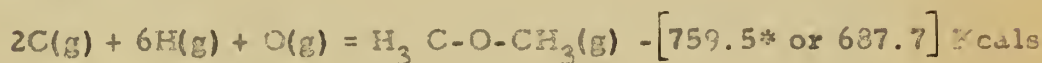


$$2C(g) = 2C(gr) - [343.3^* \text{ or } 271.6]$$

$$6H(g) = 3H_2(g) - 312.6$$

$$O(g) = 1/2 O_2(g) - 59.2$$

By addition

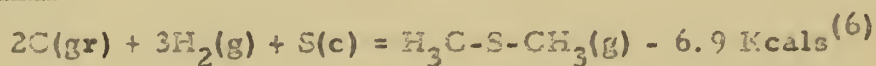


$$\xi = 6D(C-H) + 2D(C-O)$$

$$D(C-O)^* = 1/2 [759.5 - 6(98.1)] = 85.4 \text{ Kcals}^*$$

$$D(C-O) = 1/2 [687.7 - 6(89.1)] = 76.6 \text{ Kcals}$$

10. D(C-S)



$$2C(g) = 2C(gr) - [343.4 \text{ or } 271.6]$$

$$6H(g) = 3H_2(g) - 312.6$$

$$S(g) = S(c) - 53.25$$

By addition



$$\xi = 6D(C-H) + 2D(C-S)$$

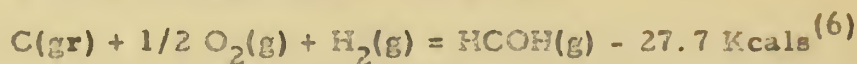
$$D(C-S)^* = 1/2 [716.15 - 6(98.1)] = 63.7 \text{ Kcals}^*$$

$$D(C-S) = 1/2 [644.35 - 6(89.1)] = 54.9 \text{ Kcals}$$



11. D(C=O)

(a) From Formaldehyde $\left(\text{H} - \overset{\text{H}}{\underset{|}{\text{C}}} = \text{O} \right)$



$$\text{C}(\text{g}) = \text{C}(\text{gr}) - [171.7* \text{ or } 135.8]$$

$$\text{O}(\text{g}) = 1/2 \text{O}_2(\text{g}) - 59.2$$

$$2\text{H}(\text{g}) = \text{H}_2(\text{g}) - 104.2$$

By addition

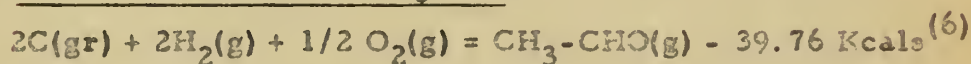


$$\{ = 2\text{D}(\text{C}-\text{H}) + \text{D}(\text{C}=\text{O})$$

$$\text{D}(\text{C}=\text{O})^* = 362.8 - 2(98.1) = 166.6 \text{ Kcals}^*$$

$$\text{D}(\text{C}=\text{O}) = 326.9 - 2(89.1) = 148.7 \text{ Kcals.}$$

(b) From Acetaldehyde $[\text{CH}_3\text{CHO}]$



$$2\text{C}(\text{g}) = 2\text{C}(\text{gr}) - [343.4* \text{ or } 271.6]$$

$$4\text{H}(\text{g}) = 2\text{H}_2(\text{g}) - 208.4$$

$$\text{O}(\text{g}) = 1/2 \text{O}_2(\text{g}) - 59.2$$

By addition



$$\{ = \text{D}(\text{C}-\text{C}) + \text{D}(\text{C}=\text{O}) + 4\text{D}(\text{C}-\text{H})$$

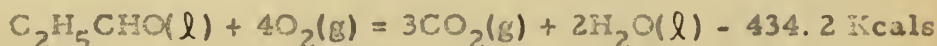
$$\text{D}(\text{C}=\text{O})^* = 650.7 - 85.5 - 4(98.1) = 172.8 \text{ kcals}^*$$

$$\text{D}(\text{C}=\text{O}) = 578.9 - 67.6 - 4(89.1) = 154.9 \text{ Kcals.}$$



(c) From Propionaldehyde (C_2H_5CHO)

The heat of combustion of the liquid and the boiling point are known to be 434.2 Kcals/mole⁽⁴⁾ and 322.0°K⁽⁴⁾ respectively. The equation for the heat of combustion is



where

$$-434.2 = 3\Delta H_f^\circ [CO_2(g)] + 2\Delta H_f^\circ [H_2O(l)] - \Delta H_f^\circ [C_2H_5CHO(l)] .$$

Solving this equation it is found that

$$\Delta H_f^\circ [C_2H_5CHO(l)] = - 52.9 \text{ Kcals,}$$

and, since by Trouton's Rule it is known that

$$\Delta H_{\text{vap}} = 21 T_{\text{B. Pt.}} = 6.76 \text{ Kcals,}$$

the heat of formation of the gaseous molecule is determined to be

$$\Delta H_f^\circ [C_2H_5CHO(g)] = - 52.9 + 6.76 = - 46.1 \text{ Kcals.}$$

Thus

$$3C(\text{gr}) + 3H_2(g) + 1/2 O_2(g) = C_2H_5CHO(g) - 46.1 \text{ Kcals}$$

$$3C(g) = 3C(\text{gr}) - [515.1^* \text{ or } 407.4]$$

$$6H(g) = 3H_2(g) - 312.6$$

$$O(g) = 1/2 O_2(g) - 59.2$$

$$3C(g) + 6H(g) + O(g) = C_2H_5CHO(g) - [933.0^* \text{ or } 825.3] \text{ Kcals}$$

$$\{ = 2D(C-C) + 6D(C-H) + D(C=O)$$

$$D(C=O)^* = 933.0 - 171.0 - 588.6 = 173.4 \text{ Kcals}^*$$

$$D(C=O) = 825.3 - 135.2 - 534.6 = 155.5 \text{ Kcals.}$$



(d) From Heptaldehyde $[\text{CH}_3(\text{CH}_2)_5 \text{CHO}]$

The heat of combustion and boiling point are known to be 1062.4 Kcals/mole⁽⁴⁾ and 428.2°K⁽⁴⁾ respectively. By a procedure similar to the previous calculation

$$\begin{aligned} Q &= -1062.4 = \Delta H_f^\circ [\text{CO}_2(\text{g})] + \Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] \\ &\quad - \Delta H_f^\circ [\text{CH}_3(\text{CH}_2)_5 \text{CHO}(\text{l})] \\ \Delta H_f^\circ [\text{CH}_3(\text{CH}_2)_5 \text{CHO}(\text{l})] &= -74.2 \text{ Kcals.} \end{aligned}$$

Since

$$\Delta H_{\text{vap}} = 21 T_{\text{B. Pt.}} = 8.98 \text{ Kcals,}$$

it is found that

$$\Delta H_f^\circ(\text{g}) = -74.2 + 8.98 = -65.2 \text{ Kcals.}$$

Thus

$$7\text{C}(\text{gr}) + 7\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{CH}_3(\text{CH}_2)_5 \text{CHO}(\text{g}) - 65.2 \text{ Kcals}$$

$$7\text{C}(\text{g}) = 7\text{C}(\text{gr}) - [1201.9^* \text{ or } 950.6]$$

$$14\text{H}(\text{g}) = 7\text{H}_2(\text{g}) - 729.4$$

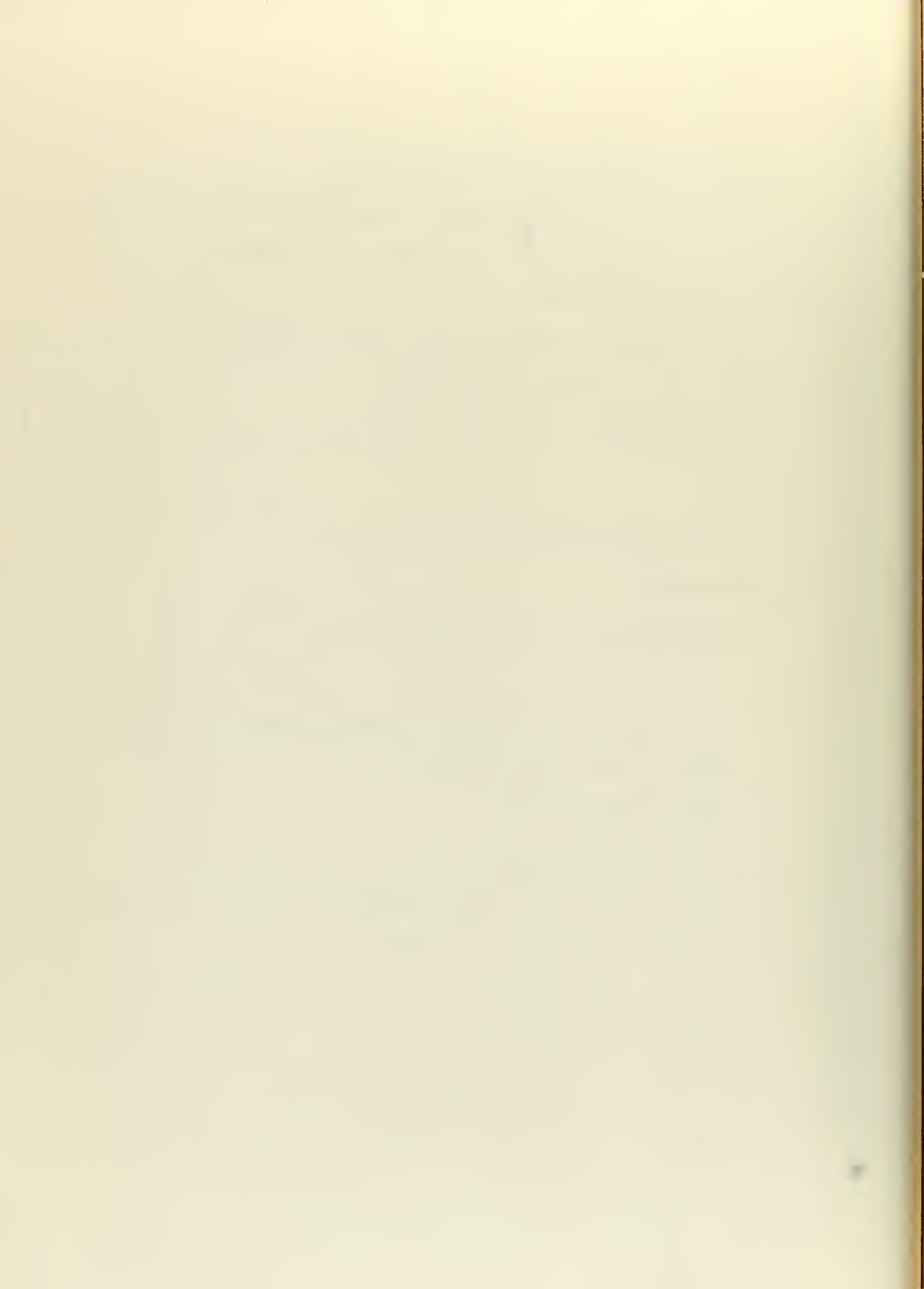
$$\text{O}(\text{g}) = 1/2 \text{O}_2(\text{g}) - 59.2$$

$$7\text{C}(\text{g}) + 14\text{H}(\text{g}) + \text{O}(\text{g}) = \text{CH}_3(\text{CH}_2)_5 \text{CHO}(\text{g}) - [2055.7^* \text{ or } 1804.4] \text{ Kcals}$$

$$\xi = 6\text{D}(\text{C}-\text{C}) + 14\text{D}(\text{C}-\text{H}) + \text{D}(\text{C}=\text{O})$$

$$\text{D}(\text{C}=\text{O})^* = 169.3 \text{ Kcals}^*$$

$$\text{D}(\text{C}=\text{O}) = 151.4 \text{ Kcals}$$



Averaging the values for the higher aldehydes, it is found that

$$C(C=O)^* = 171.8 \text{ Kcals}^*$$

$$D(C=O) = 153.9 \text{ Kcals}$$

(e) From Diethyl ketone $[(C_2H_5)_2 CO]$

The heat of combustion in the liquid state and the boiling point temperature are 735.6 Kcals/mole⁽⁴⁾ and 102.7°C. respectively.

From the equation for the combustion of this compound, it can be written that

$$\begin{aligned} \Delta H_f^0 [(C_2H_5)_2 CO(l)] &= - Q + 5\Delta H_f^0 [CO_2(g)] + 5\Delta H_f^0 [H_2O(l)] \\ &= - 76.25 \text{ Kcals.} \end{aligned}$$

Since it is known by Trouton's Rule that

$$\Delta H_{vap} = 21 T_{B. Pt.} = 7.89 \text{ Kcals,}$$

it is found that

$$\Delta H_f^0(g) = - 68.4 \text{ Kcals.}$$

Thus

$$5C(gr) + 5H_2(g) + 1/2 O_2(g) = (C_2H_5)_2 CO(g) - 68.4 \text{ Kcals}$$

$$5C(g) = 5C(gr) - [858.5^* \text{ or } 679.0]$$

$$10H(g) = 5H_2(g) - 521.0$$

$$O(g) = 1/2 O_2(g) - 59.2$$

$$5C(g) + 10H(g) + O(g) = (C_2H_5)_2 CO(g) - [1507.1 \text{ or } 1327.6] \text{ Kcals}$$

$$\{ = 4D(C-C) + 10D(C-H) + D(C=O)$$

$$D(C=O)^* = 184.1 \text{ Kcals}^*$$

$$D(C=O) = 166.2 \text{ Kcals.}$$



(f) From Methyl-propyl ketone $[(CH_3)(C_3H_7)CO]$

The heat of combustion in the liquid state and the boiling point are 735.6 Kcals/mole⁽⁴⁾ and 101.7°C.⁽⁴⁾ respectively. From the combustion equation, it is seen that

$$\Delta H_f^\circ(l) = -Q + 5\Delta H_f^\circ[CO_2(g)] + 5\Delta H_f^\circ[H_2O(l)] = -76.3 \text{ Kcals.}$$

Since

$$\Delta H_{vap} = 21(T_{B.Pt}) = 7.9 \text{ Kcals,}$$

it is found that

$$\Delta H_f^\circ[(CH_3)(C_3H_7)CO(g)] = -68.4 \text{ Kcals.}$$

Thus

$$5C(gr) + 5H_2(g) + 1/2 O_2(g) = (CH_3)(C_3H_7)CO(g) - 68.4 \text{ Kcals}$$

$$5C(g) = 5C(gr) - [858.5* \text{ or } 679.0]$$

$$10H(g) = 5H_2(g) - 521.0$$

$$O(g) = 1/2 O_2(g) - 59.2$$

$$5C(g) + 10H(g) + O(g) = (CH_3)(C_3H_7)CO(g) - [1507.1 \text{ or } 1327.6] \text{ Kcals.}$$

$$\{ = 4D(C-C) + 10D(C-H) + D(C=O)$$

$$D(C=O)* = 184.1 \text{ Kcals*}$$

$$D(C=O) = 166.2 \text{ Kcals.}$$

(g) Di propyl ketone $[(C_3H_7)_2CO]$

The heat of combustion of the liquid and the boiling point are 1050.5 Kcals/mole⁽⁴⁾ and 144°C.⁽⁴⁾ respectively. From the combustion



equation it can be written

$$\Delta H_f^{\circ}(\ell) = -Q + 7\Delta H_f^{\circ}[\text{CO}_2(\text{g})] + 7\Delta H_f^{\circ}[\text{H}_2\text{O}(\ell)]$$

$$\Delta H_f^{\circ}(\ell) = -86.1 \text{ Kcals.}$$

The heat of vaporization by Trouton's Rule is

$$\Delta H_{\text{vap}} = 21(T_{\text{B. Pt.}}) = 3.8 \text{ Kcals}$$

so that

$$\Delta H_f^{\circ}(\text{g}) = -77.3 \text{ Kcals}$$

Thus

$$7\text{C}(\text{gr}) + 7\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = (\text{C}_3\text{H}_7)_2 \text{CO}(\text{g}) - 77.3 \text{ Kcals}$$

$$7\text{C}(\text{g}) = 7\text{C}(\text{gr}) - [1201.9* \text{ or } 950.6]$$

$$14\text{H}(\text{g}) = 7\text{H}_2(\text{g}) - 729.4$$

$$\text{O}(\text{g}) = 1/2 \text{O}_2(\text{g}) - 59.2$$

$$7\text{C}(\text{g}) + 14\text{H}(\text{g}) + \text{O}(\text{g}) = (\text{C}_3\text{H}_7)_2 \text{CO}(\text{g}) - [2067.8* \text{ or } 1816.5] \text{ Kcals}$$

$$\xi = 6\text{D}(\text{C}-\text{C}) + 14\text{D}(\text{C}-\text{H}) + \text{D}(\text{C}=\text{O})$$

$$\text{D}(\text{C}=\text{O})^* = 181.4 \text{ Kcals}^*$$

$$\text{D}(\text{C}=\text{O}) = 163.5 \text{ Kcals.}$$

Averaging the values for the ketones, it is found that

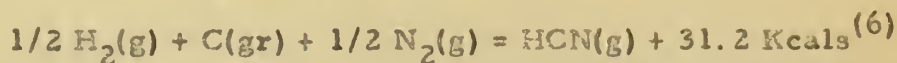
$$\text{D}(\text{C}=\text{O})^* = 183.2 \text{ Kcals}^*$$

$$\text{D}(\text{C}=\text{O}) = 165.3 \text{ Kcals.}$$



12. D(C≡N)

(a) From Hydrogen Cyanide (HCN)



$$\text{H}(\text{g}) = 1/2 \text{H}_2(\text{g}) - 52.1$$

$$\text{C}(\text{g}) = \text{C}(\text{gr}) - [171.7^* \text{ or } 135.8]$$

$$\text{N}(\text{g}) = 1/2 \text{N}_2(\text{g}) = 112.8$$

$$\text{H}(\text{g}) + \text{C}(\text{g}) + \text{N}(\text{g}) = \text{NCN}(\text{g}) - [305.4^* \text{ or } 269.5] \text{ Kcals}$$

$$\xi = \text{D}(\text{C}-\text{H}) + \text{D}(\text{C}\equiv\text{N})$$

$$\text{D}(\text{C}\equiv\text{N})^* = 207.3 \text{ Kcals}^*$$

$$\text{D}(\text{C}\equiv\text{N}) = 180.4 \text{ Kcals.}$$

(b) From Methyl Cyanide

The heat of combustion of the liquid and the heat of vaporization are 302.4 Kcals/mole⁽⁴⁾ and 7.0 Kcals/mole respectively. From the combustion equation, it is seen that

$$\begin{aligned} \Delta \text{Hf}^\circ [\text{CH}_3 \text{CN}(\text{l})] &= -Q + 2\Delta \text{Hf}^\circ [\text{CO}_2(\text{g})] \\ &+ 3/2 \Delta \text{Hf}^\circ [\text{H}_2\text{O}(\text{l})] = 11.8 \text{ Kcals.} \end{aligned}$$

Therefore, it is found that

$$\Delta \text{Hf}^\circ [\text{CH}_3 \text{CN}(\text{g})] = 18.8 \text{ Kcals.}$$

Thus

$$2\text{C}(\text{gr}) + 3/2 \text{H}_2(\text{g}) + 1/2 \text{N}_2(\text{g}) = \text{CH}_3 \text{CN}(\text{g}) + 18.8 \text{ Kcals}$$

$$2\text{C}(\text{g}) = 2\text{C}(\text{gr}) - [343.4^* \text{ or } 271.6]$$

$$3\text{H}(\text{g}) = 3/2 \text{H}_2(\text{g}) - 156.3$$

$$\text{N}(\text{g}) = 1/2 \text{N}_2(\text{g}) - 112.8$$

$$2\text{C}(\text{g}) + 3\text{H}(\text{g}) + \text{N}(\text{g}) = \text{CH}_3 \text{CN}(\text{g}) - [593.7^* \text{ or } 521.9] \text{ Kcals}$$



$$\xi = D(C\equiv N) + 3D(C-H) + D(C-C)$$

$$D(C\equiv N)^* = 213.9 \text{ Kcals}^*$$

$$D(C\equiv N) = 187.0 \text{ Kcals.}$$

The average of the foregoing bond energies are

$$D(C\equiv N)^* = 210.6 \text{ Kcals}^*$$

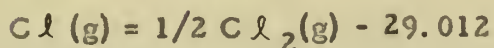
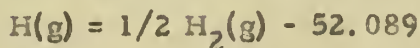
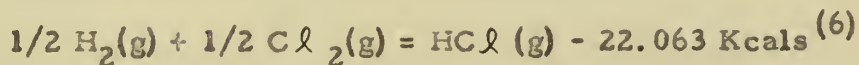
$$D(C\equiv N) = 183.7 \text{ Kcals.}$$



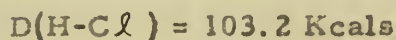
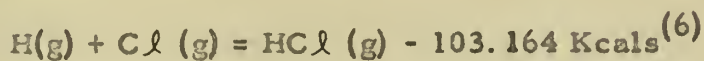
APPENDIX II

SUMMARY OF CALCULATIONS USED TO DETERMINE BOND ENERGIES NOT INVOLVING CARBON

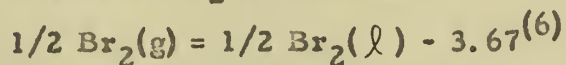
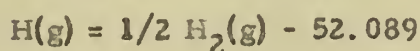
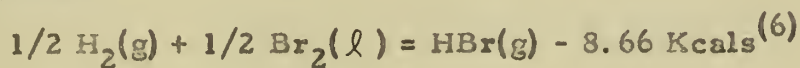
1. D(H-Cl)



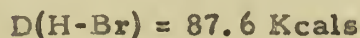
By addition



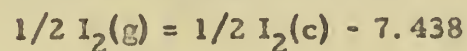
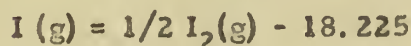
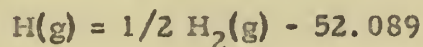
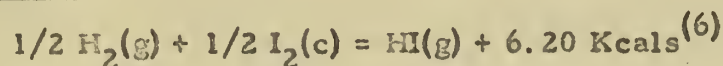
2. D(H-Br)



By addition

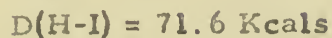
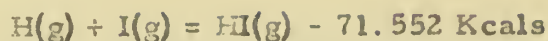


3. D(H-I)

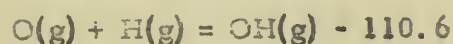
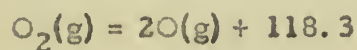
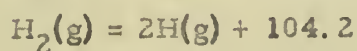
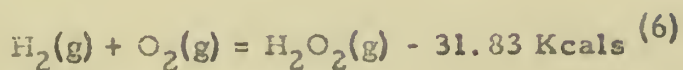




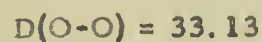
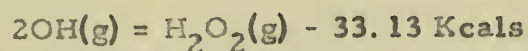
By addition



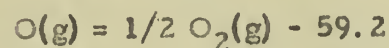
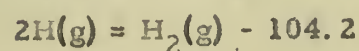
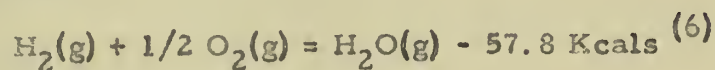
4. D(O-O)



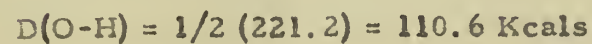
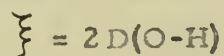
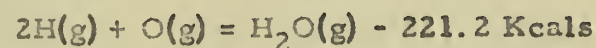
By addition



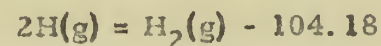
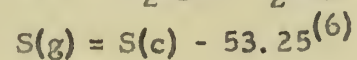
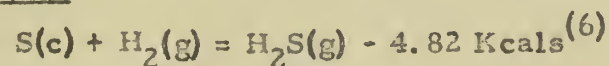
5. D(O-H)



By addition

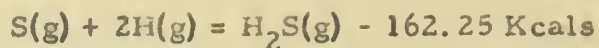


6. D(H-S)





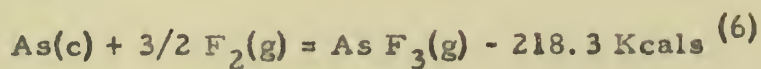
By addition



$$\xi = 2 \text{ D(H-S)}$$

$$\text{D(H-S)} = 1/2 (162.25) = 81.1 \text{ Kcals}$$

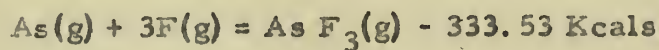
7. D(As-F)



$$\text{As(g)} = \text{As(c)} = 60.64 \quad (6)$$

$$3\text{F(g)} = 3/2 \text{ F}_2(\text{g}) - 54.59$$

By addition



$$= 3 \text{ D(As-F)}$$

$$\text{D(As-F)} = 111.2 \text{ Kcals}$$

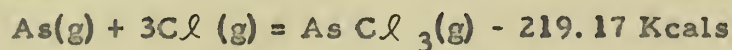
8. D(As-Cl)



$$\text{As(g)} = \text{As(c)} = 60.64 \quad (6)$$

$$3\text{Cl(g)} = 3/2 \text{ Cl}_2(\text{g}) - 87.03$$

By addition



$$\xi = 3 \text{ D(As-Cl)}$$

$$\text{D(As-Cl)} = 73.1 \text{ Kcals}$$

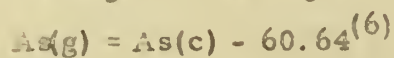
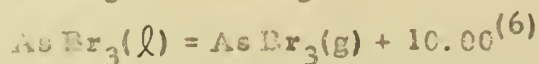
9. D(As-Br)



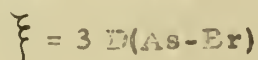
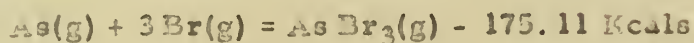
$$3/2 \text{ Br}_2(\text{g}) = 3/2 \text{ Br}_2(\ell) - 11.01 \quad (6)$$



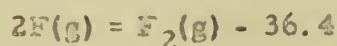
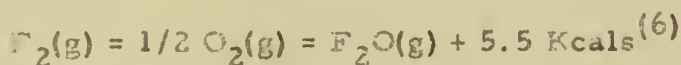
9. D(As-Br) (Continued)



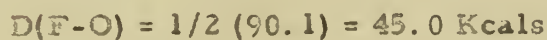
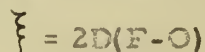
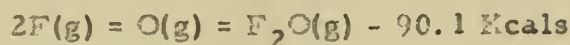
By addition



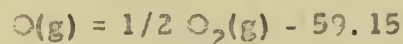
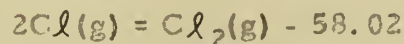
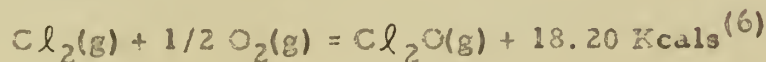
10. D(F-O)



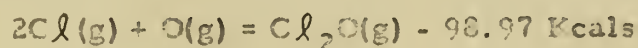
By addition



11. D(Cl-O)

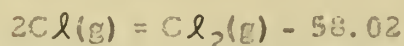
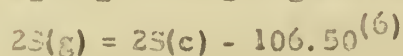
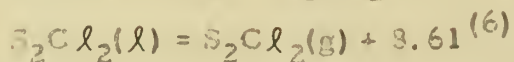
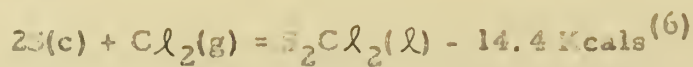


By addition

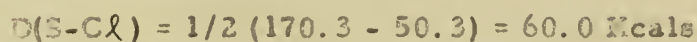
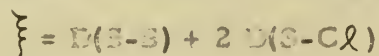
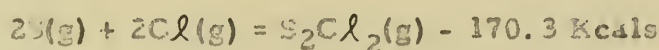




12. D(S-Cl)



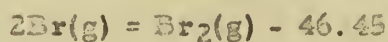
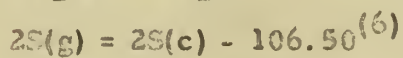
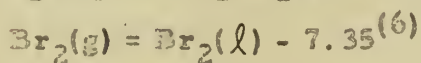
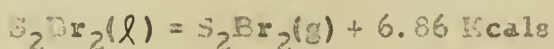
By addition



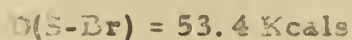
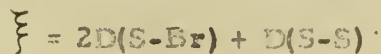
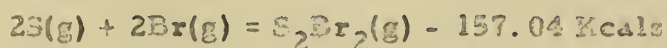
13. D(S-Br)



The heat of vaporization is estimated by Trouton's Rule to be

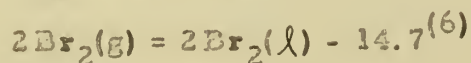
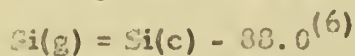


By addition

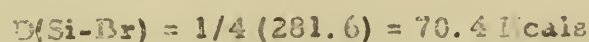
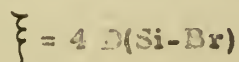
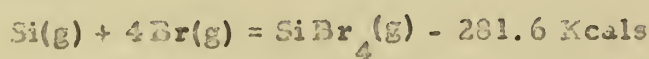




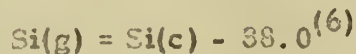
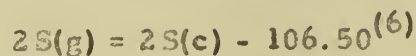
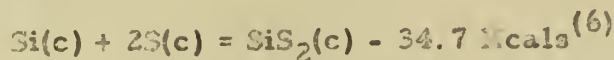
14. D(Si-Br)



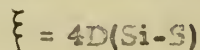
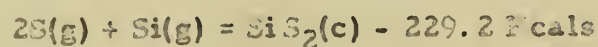
By addition



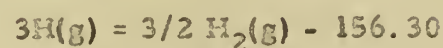
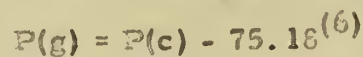
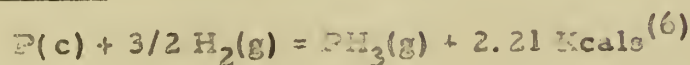
15. D(Si-S)



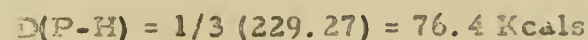
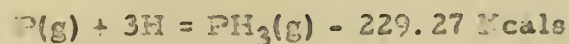
By addition



16. D(P-H)

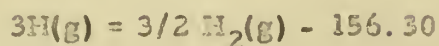
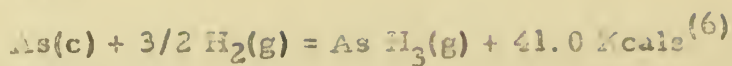


By addition

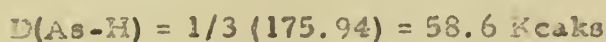
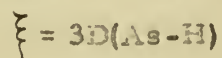
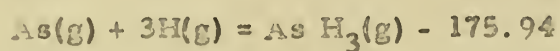




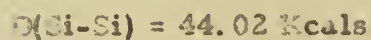
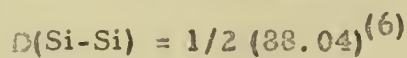
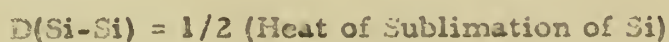
17. D(As-H)



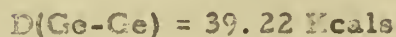
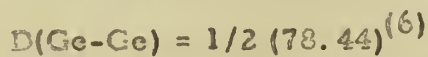
By addition



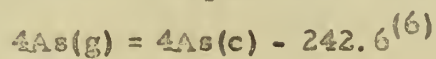
18. D(Si-Si)



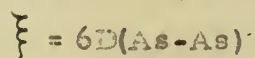
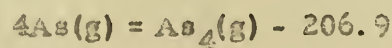
19. D(Ge-Ge)



20. D(As-As)

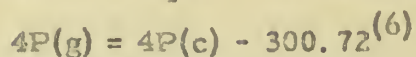
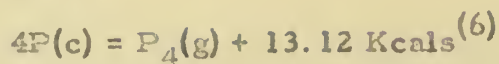


By addition

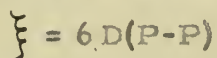
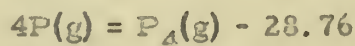




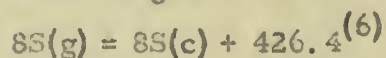
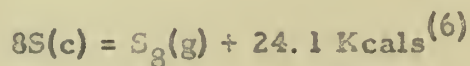
21. D(P-P)



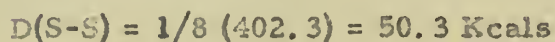
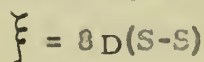
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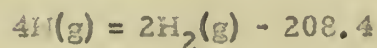
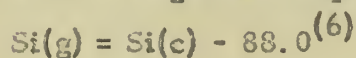
22. D(S-S)



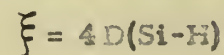
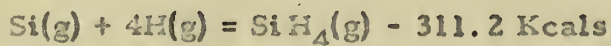
By addition



23. D(Si-H)

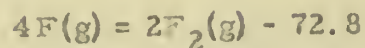
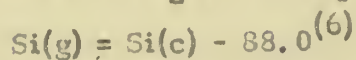
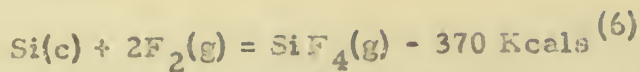


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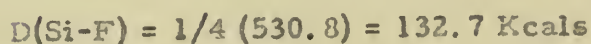
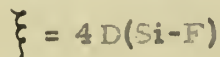
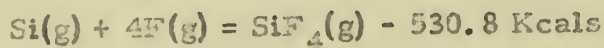




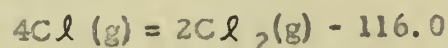
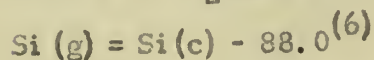
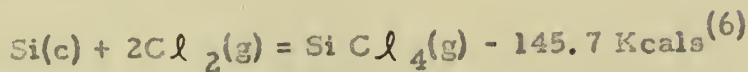
24. D(Si-F)



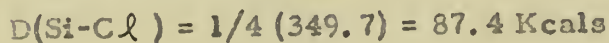
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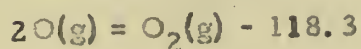
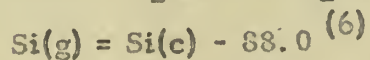
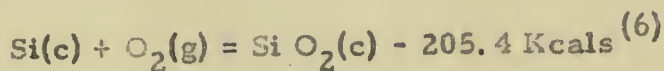
25. D(Si-Cl)



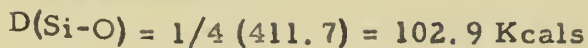
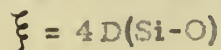
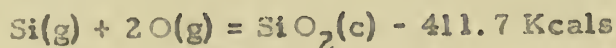
By addition



26. D(Si-O)

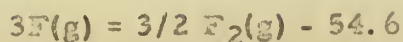
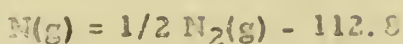


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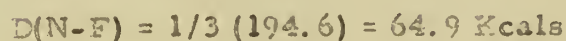
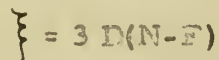




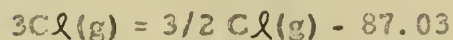
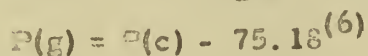
27. D(N-F)



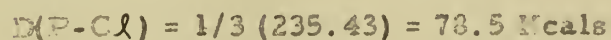
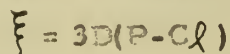
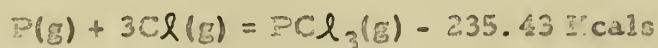
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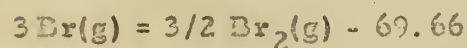
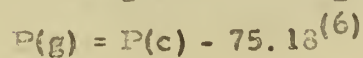
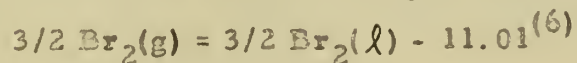
28. D(P-Cl)



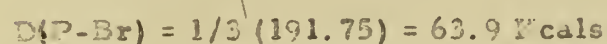
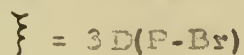
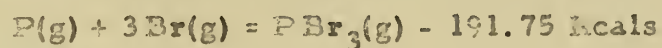
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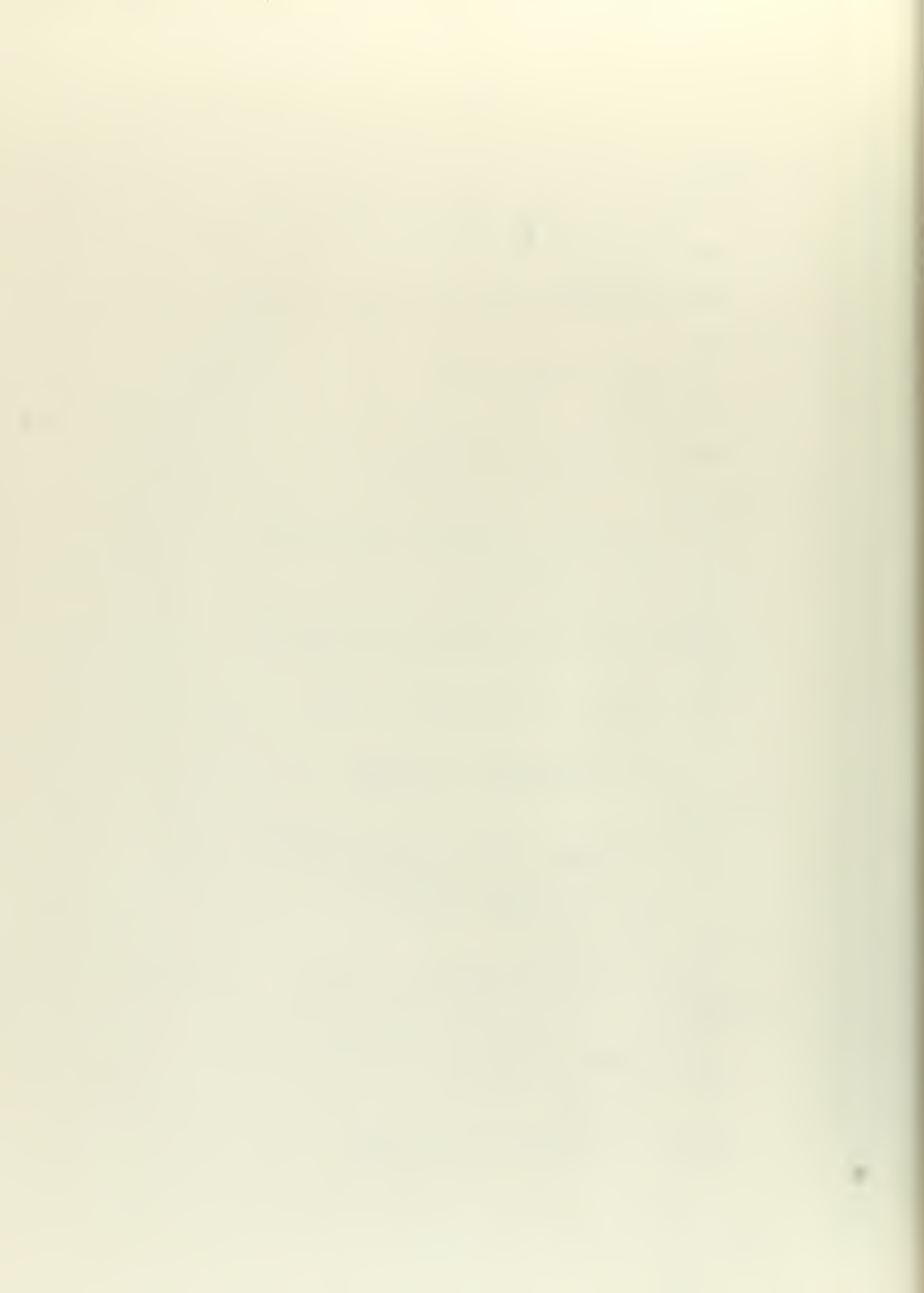


29. D(P-Br)



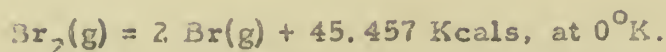
By addition





30. D(Br-Br)

Since it is known that $D(\text{Br-Br})^{\circ} = 45.457 \text{ Kcals}$, ^(8a) it can be written that



The correction of the bond energy value from 0°K to 298.16°K is found through use of the equation

$$D(\text{Br-Br}) = D(\text{Br-Br})^{\circ} + \Delta \left[RT^2 d \ln Q_{\text{vib}}/dT \right] + \Delta (5/2 RT)^{(7)}$$

where

$$\Delta (RT^2 d \ln Q_{\text{vib}}/dT) = RT^2 \left\{ - \left[d \ln Q_{\text{vib}}/dT \right]_{\text{Br}_2} + 2 \left[d \ln Q_{\text{vib}}/dT \right]_{\text{Br}} \right\}.$$

But since $\left[d \ln Q_{\text{vib}}/dT \right]_{\text{Br}} = 0$, it is seen that

$$\Delta \left[RT^2 d \ln Q_{\text{vib}}/dT \right] = -RT^2 \left[d \ln Q_{\text{vib}}/dT \right]_{\text{Br}_2} = -RT u \left[\exp u - 1 \right]_{\text{Br}_2}^{-1}$$

where $u_{\text{Br}_2} = hc \omega^*/kT = 0.02695 \text{ radians}$. ^(3b) Evaluating this quantity one obtains

$$\Delta RT^2 d \ln Q_{\text{vib}}/dT = -0.986 RT$$

The correction may now be completed since it can be written that

$\Delta 5/2 RT = +5/2 RT$, since Δ is the change in number of moles for the above reaction, and therefore

$$D(\text{Br-Br}) = 45.457 + 5/2 RT - 0.986 RT$$

$$D(\text{Br-Br}) = 46.444 \text{ Kcals.}$$

31. D(I-I)

Since it is known that $D(\text{I-I})^{\circ} = 35.556 \text{ Kcals}$ ^(8a), the following equation can be written, viz.,



$$1/2(g) = 21(g) + 35.556 \text{ Kcals, at } 0^\circ\text{K.}$$

The correction of the bond energy value from 0°K to 298.16°K is carried out by exactly the same procedure as before, so that

$$D(I-I) = D(I-I)^0 + \Delta [RT^2 d \ln Q_{\text{vib}}/dT] + \Delta [5/2 RT]$$

where

$$\Delta [RT^2 d \ln Q_{\text{vib}}/dT] = -RT^2 [d \ln Q_{\text{vib}}/dT]_{I_2} = -RTu [\exp(-i)]_{I_2}^{-1}$$

and $u_{I_2} = 0.01788 \text{ radians.}^{(3b)}$ One obtains upon evaluation

that $\Delta [RT^2 d \ln Q_{\text{vib}}/dT] = -0.991 RT$, and from the above equation,

that $\Delta [5/2 RT] = + 5/2 RT$. Thus it is seen that

$$D(I-I) = 35.556 + 5/2 RT - 0.991 RT$$

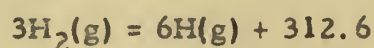
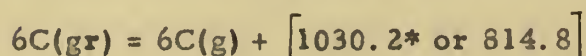
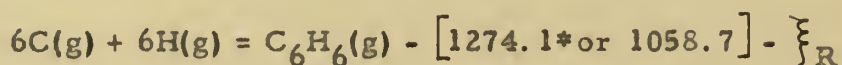
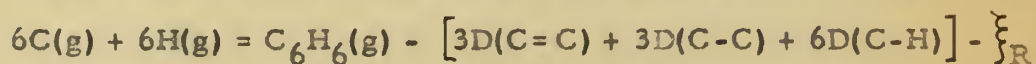
$$D(I-I) = 36.450 \text{ Kcals.}$$

APPENDIX III

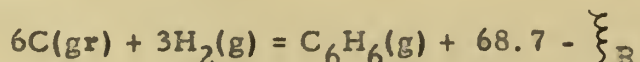
RESONANCE CALCULATIONS

1. Benzene (C₆H₆)

The standard heat of formation is known to be 19.82 kcal/mole. ⁽⁶⁾



By addition



$$\xi_R = -19.82 + 68.7 = 48.9 \text{ kcal}$$

2. Naphthalene (C₁₀H₈)

The heat of combustion of the compound in the crystalline state, the heat of fusion, and the heat of vaporization are 1232.5 kcal/mole, ⁽⁴⁾ 4.65 kcal/mole, ⁽⁴⁾ and 9.65 kcal/mole, ⁽⁴⁾ respectively.

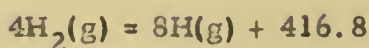
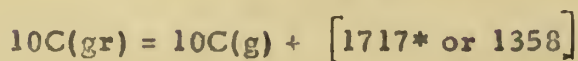
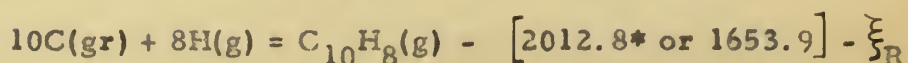
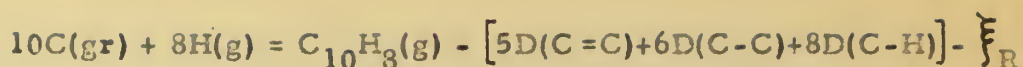
From the combustion equation, it can be written that

$$\Delta H_f^\circ(c) = -Q + 10 \Delta H_f^\circ [CO_2(g)] + 4 \Delta H_f^\circ [H_2O(l)] = +18.7 \text{ kcal},$$

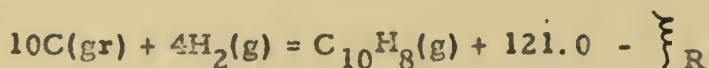
so that

$$\Delta H_f^\circ(g) = +18.7 + 4.65 + 9.65 = 33.0 \text{ kcal}$$

Thus



By addition



$$\xi_R = 88.0 \text{ kcal}$$

3. Aniline ($C_6H_5NH_2$)

The standard heat of formation of the compound in the liquid state and the boiling point are $-4.451 \text{ kcal/mole}^{(4)}$ and $457.6^\circ\text{K}^{(4)}$ respectively. The heat of vaporization is estimated by Trouton's rule as follows,

$$\Delta H_{\text{vap}} = 21 T_{\text{B.pt}} = 9.6 \text{ kcal},$$

so that

$$\Delta H_f^\circ |C_6H_5NH_2(\text{g})| = -4.451 + 9.6 = 5.1 \text{ kcal}$$

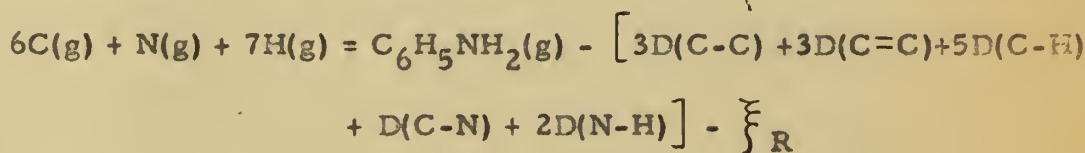
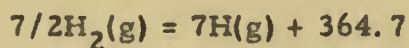
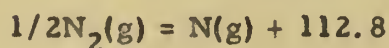
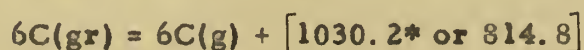
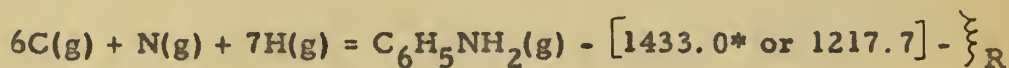


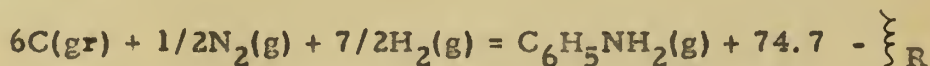
Table A-V. Data Used for Computation of \sum_R for Aniline

Bond	Bond Energy	
	L(C) + 171.1	L(C) = 135.8
3D(C-C)	256.5	202.8
3D(C=C)	429.0	321.3
5D(C-H)	490.5	445.5
D(C-N)	81.0	72.1
2D(N-H)	<u>176.0</u>	<u>176.0</u>
Total (\sum)	1433.0	1217.7

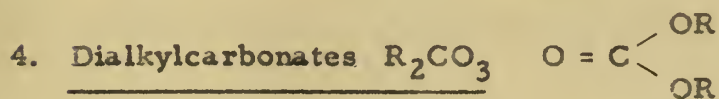
Thus



By addition



$$\sum_R = 74.7 - 5.1 = 69.6 \text{ kcal}$$



(a) From dimethyl carbonate. The heat of combustion in the liquid state is 340.8 kcal/mole. (4) From the combustion equation it is seen that

$$\begin{aligned}\Delta H_f^\circ [(\text{CH}_3)_2 \text{CO}_3(l)] &= -Q + 3\Delta H_f^\circ [\text{CO}_2(g)] + 3\Delta H_f^\circ [\text{H}_2\text{O}(l)] \\ &= -146.3 \text{ kcal/s}\end{aligned}$$

It is also known that

$$\Delta H_{\text{vap}} = 7.9 \text{ kcal/s},^{(4)}$$

so that

$$\Delta H_f^\circ [(\text{CH}_3)_2 \text{CO}_3(g)] = -138.4 \text{ kcal/s}$$

$$3\text{C}(g) + 6\text{H}(g) + 3\text{O}(g) = (\text{CH}_3)_2 \text{CO}_3 - [\text{D}(\text{C}=\text{O}) + 4\text{D}(\text{C}-\text{O}) + 6\text{D}(\text{C}-\text{H})] - \xi_R$$

Table A-VI. Data Used for Computation of ξ_R for $(\text{CH}_3)_2 \text{CO}_3$

Bond	Bond Energy	
	L(C) = 171.7	L(C) = 135.8
D(C=O)	183.2	165.3
4D(C-O)	341.6	306.4
6D(C-H)	<u>588.6</u>	<u>534.6</u>
Total	1113.4	1006.3

Thus

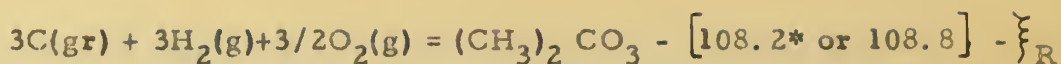
$$3\text{C}(g) + 6\text{H}(g) + 3\text{O}(g) = (\text{CH}_3)_2 \text{CO}_3(g) - [1113.4^* \text{ or } 1006.3] - \xi_R$$

$$3\text{C}(gr) = 3\text{C}(g) + [515.1^* \text{ or } 407.4]$$

$$3\text{H}_2(g) = 6\text{H}(g) + 312.6$$

$$3/2 \text{O}_2(g) = 3\text{O}(g) + 177.5$$

By addition



$$\xi_R = +138.4 - 108.5 = 29.9 \text{ kcal}$$

(b) Diethyl carbonate

The heat of combustion of the liquid and the boiling point are 467.9 kcal/mole⁽⁴⁾ and 399.0°K respectively. From the combustion equation, it can be written

$$\begin{aligned}\Delta H_f^\circ [(C_2H_5)_2CO_3(l)] &= -Q + 5\Delta H_f^\circ [CO_2(g)] + 5\Delta H_f^\circ [H_2O(l)] \\ &= -164.0 \text{ kcal}\end{aligned}$$

It may be estimated that

$$\Delta H_{\text{vap}} = 21 (T_{\text{B.pt}}) = 8.4 \text{ kcal}$$

so that

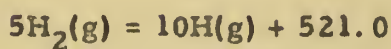
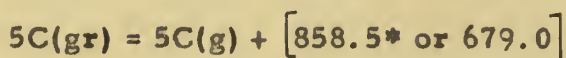
$$\Delta H_f^\circ (C_2H_5)_2CO_3(g) = -164.0 + 8.4 = -155.6 \text{ kcal}$$

$$\begin{aligned}5C(\text{g}) + 10H(\text{g}) + 3O(\text{g}) &= (C_2H_5)_2CO_3(\text{g}) - [2D(C-C) + 4D(C-O) \\ &\quad + D(C=O) + 10D(C-H)] - \xi_R\end{aligned}$$

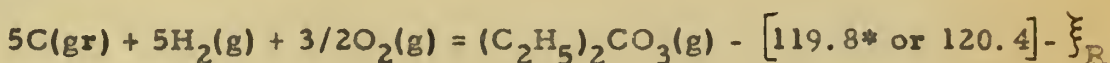
Table A-VII. Data Used for Computation of ξ_R for $(C_2H_5)_2CO_3$

Bond	Bond Energy	
	L(C) = 171.7	L(C) = 135.8
2D(C-C)	171.0	135.2
4D(C-O)	341.6	306.4
D(C=O)	183.2	165.3
10D(C-H)	981.0	891.0
Total	1676.8	1497.9

Thus



By addition



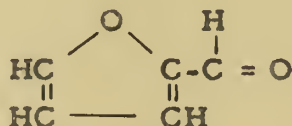
$$\xi_R = 155.6 - 1/2 (119.8 + 120.4)$$

$$\xi_R = 35.5 \text{ kcal}$$

The average of the two computations is

$$\xi_R = 32.7 \text{ kcal}$$

5. Furfural



The heat of combustion of the liquid and the heat of vaporization are 559.5 kcal/mole⁽⁴⁾ and 10.31 kcal/mole,⁽⁴⁾ respectively. From the combustion equation, it is seen that

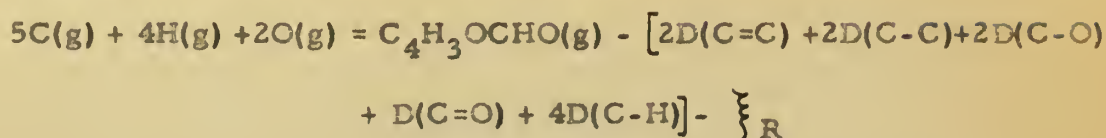
$$\Delta H_f^\circ [C_4H_3OCHO(l)] = -Q(l) + 5\Delta H_f^\circ [CO_2(g)] + 2\Delta H_f^\circ [H_2O(l)]$$

$$\Delta H_f^\circ(l) = 5(-94.05) + 2(-68.32) + 559.5$$

$$\Delta H_f^\circ(l) = -47.4 \text{ kcal}$$

Therefore the heat of formation of the gaseous molecule is

$$\Delta H_f^O(g) = - 47.4 + 10.3 = - 37.1 \text{ kcal}$$

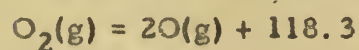
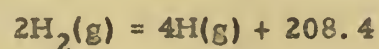
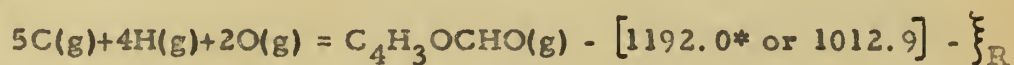


The value of $D(C=O)$ for higher aldehydes will be used because of structural considerations.

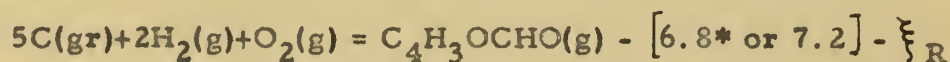
Table A-VIII. Data Used for Computation of ξ_R for Furfural

Bond	Bond Energy	
	$L(C) = 171.7$	$L(C) = 135.8$
$2D(C=C)$	286.0	214.2
$2D(C-C)$	171.0	135.2
$2D(C-O)$	170.8	153.2
$D(C=O)$	171.8	153.9
$4D(C-H)$	<u>392.4</u>	<u>356.4</u>
Total	1192.0	1012.9

Thus



By addition



$$\xi_R = + 37.1 - 1/2 (6.8 + 7.2)$$

$$\xi_R = + 37.1 - 7.0 = 30.1 \text{ kcal}$$

6. Phenyl acetylene (C_6H_5CCH)

The heat of combustion of the liquid and the boiling point are -1024.2 kcal/mole⁽⁴⁾ and $416.2^\circ K$ ⁽⁴⁾ respectively. The heat of vaporization is estimated by Trouton's rule to be

$$H_{vap} = 21 T_{B.Pt.} = 8.73 \text{ kcal.}$$

From the definition of the heat of combustion, it is seen that

$$\Delta H_f^\circ [C_6H_5CCH(l)] = 8\Delta H_f^\circ [CO_2(g)] + 3\Delta H_f^\circ [H_2O(l)] - Q$$

$$\Delta H_f^\circ (l) = 8(-94.05) + 3(-68.32) + 1024.2$$

$$\Delta H_f^\circ (l) = +66.8 \text{ kcal}$$

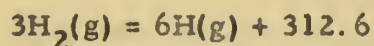
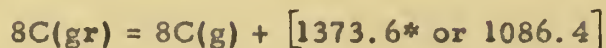
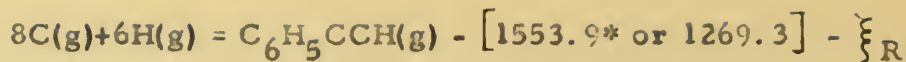
$$\Delta H_f^\circ (g) = 75.5 \text{ kcal}$$

$$8C(g) + 6H(g) = C_6H_5CCH(g) - [3D(C=C) + 4D(C-C) + D(C\equiv C) + 6D(C-H)] - \xi_R$$

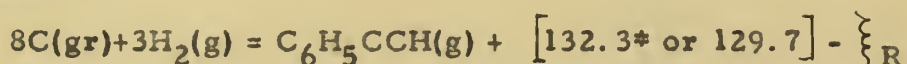
Table A-IX. Data Used for Computation of ξ_R for C_6H_5CCH

Bond	Bond Energy	
	$L(C) = 171.7$	$L(C) = 135.8$
$3D(C=C)$	429.0	321.3
$4D(C-C)$	342.0	270.4
$D(C\equiv C)$	194.3	143.0
$6D(C-H)$	<u>588.6</u>	<u>534.6</u>
Total	1553.9	1269.3

Thus



By addition



$$\xi_R = 1/2 (132.3 + 129.7) - 75.5$$

$$\xi_R = 55.5 \text{ kcal}$$

7. Phenyl cyanide (C_6H_5CN)

The heat of combustion of the liquid and the boiling point are 865.5 kcal/mole⁽⁴⁾ and 463.9°K, ⁽⁴⁾ respectively. The appropriate estimate for the heat of vaporization is

$$\Delta H_{vap} = 21T_{B.pt} = 9.73 \text{ kcal}$$

By the definition of heat of combustion, it is seen that

$$\Delta H_f^\circ [C_6H_5CN(l)] = -Q() + 7\Delta H_f^\circ [CO_2(g)] + 2.5\Delta H_f^\circ [H_2O(l)]$$

$$\Delta H_f^\circ(l) = + 36.3 \text{ kcal}$$

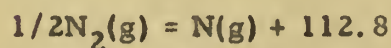
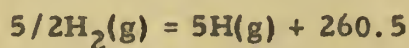
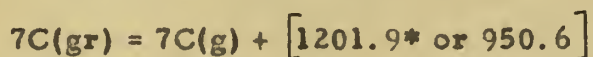
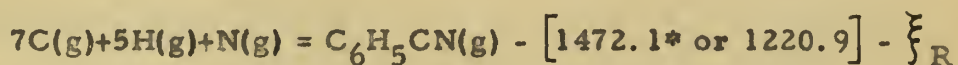
$$\Delta H_f^\circ(g) = 46.0 \text{ kcal}$$

$$7C(g) + 5H(g) + N(g) = C_6H_5CN(g) - [3D(C=C) + 4D(C-C) + D(C=N) + 5D(C-H)] - \xi_R$$

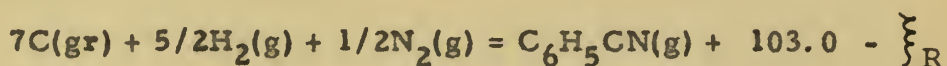
Table A-X. Data Used for Computation of \sum_R for C_6H_5CN

Bond	Bond Energy	
	$L(C) = 171.7$	$L(C) = 135.8$
3D(C=C)	429.0	321.3
4D(C-C)	342.0	270.4
D(C≡N)	210.6	183.7
5D(C-H)	<u>490.5</u>	<u>445.5</u>
Total	1472.1	1220.9

Thus



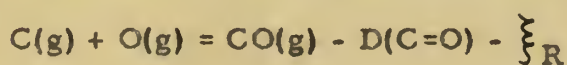
By addition



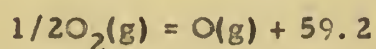
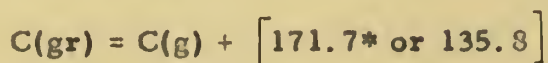
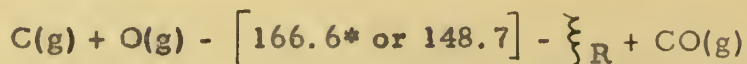
$$\sum_R = 57.0 \text{ kcal}$$

8. Carbon Monoxide (C=O)

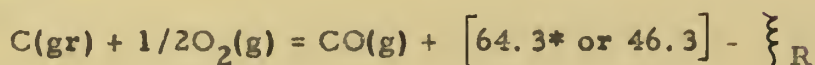
The heat of vaporization is known to be - 26.42 kcal/mole. (6)



Using $D(C=O)$ determined from formaldehyde, it is seen that



By addition

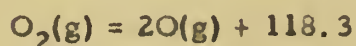
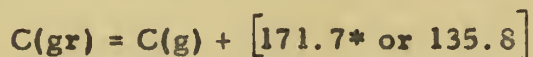
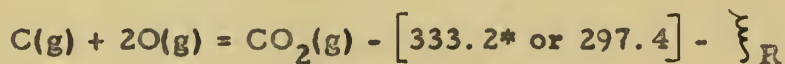
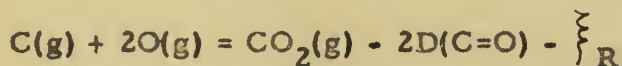


$$\xi_R^* = 90.7* \text{ kcal/s}$$

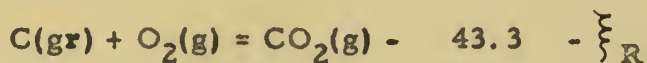
$$\xi_R = 72.7 \text{ kcal/s}$$

9. Carbon dioxide ($O=C=O$)

The heat of vaporization is $-94.05 \text{ kcal/s/mole.}^{(6)}$



By addition



$$\xi_R = 50.7 \text{ kcal/s}$$

10. Acetophenone ($C_6H_5COCH_3$)

The heat of combustion in the crystalline state, the melting and boiling points are 988.9 Kcals, ⁽⁴⁾ 292.9°K, ⁽⁴⁾ and 475.5°K⁽⁴⁾ respectively. Estimates of the heats of fusion and vaporization can be made as follows

$$\Delta H_{\text{fusion}} = 10 T_{\text{M. Pt}} = 2.9 \text{ Kcals}$$

$$\Delta H_{\text{vap}} = 21 T_{\text{B. Pt}} = 10.0 \text{ Kcals.}$$

From the equation for the combustion of this hydrocarbon, it is seen that

$$\Delta H_f^\circ [C_6H_5COCH_3(c)] = -Q(c) + 8\Delta H_f^\circ [CO_2(g)] + 4\Delta H_f^\circ [H_2O(l)]$$

$$\Delta H_f^\circ(c) = 8(-94.05) + 4(-68.32) + 988.9$$

$$\Delta H_f^\circ(c) = -36.8 \text{ Kcals}$$

$$\Delta H_f^\circ(l) = -36.8 + 2.9 = -33.9 \text{ Kcals}$$

$$\Delta H_f^\circ(g) = -33.9 + 10.0 = -23.9 \text{ Kcals}$$

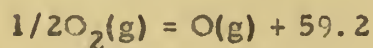
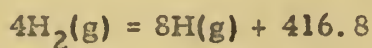
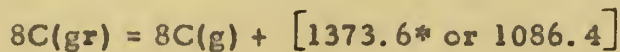
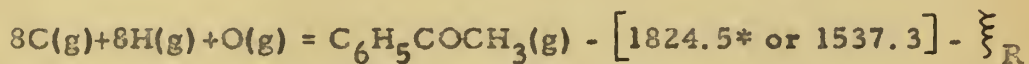
$$8C(g) + 8H(g) + O(g) = C_6H_5COCH_3(g) - [3D(C=C) + 5D(C-C) + D(C=O) + 8D(C-H)] - \xi_R$$

The $D(C=O)$ from the ketones will be used in the computation because of structural considerations.

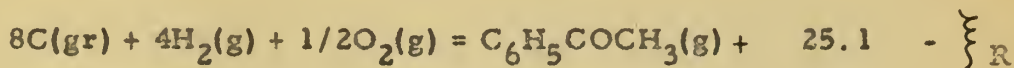
Table A-XI. Data Used for Computation of \sum_R for $C_6H_5COCH_3$

Bond	Bond Energy	
	$L(C) = 171.7$	$L(C) = 135.8$
3D(C=C)	429.0	321.3
5D(C-C)	427.5	338.0
D(C=O)	183.2	165.2
8D(C-H)	<u>784.8</u>	<u>712.8</u>
Total	1824.5	1537.3

Thus



By addition



$$\sum_R = 23.9 + 25.1 = 49.0 \text{ kcal}$$

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